Andreas Prahs · Daniel Schneider · Britta Nestler

A continuum thermodynamic approach to the phase-field method: the order parameter as internal state variable

Abstract The phase-field method is well established for simulating microstructure evolution in computational materials science, providing a numerically efficient tracking of interfaces and surfaces by means of an order parameter. The derivation of its evolution equation is usually based on a variational approach or a corresponding principle of virtual power. Both approaches consider the order parameter as an additional degree of freedom and assume a diffuse interface region from the outset. This work examines the interpretation of the order parameter as an internal state variable, instead of an additional degree of freedom, since it represents an observable rather than a controllable quantity. Furthermore, the phase-field method is considered as an approximation of the sharp interface theory of a continuum containing a singular surface. A Cauchy continuum with a material singular surface is considered as starting point. The evolution equation of the order parameter is derived consistently in the context of continuum thermodynamics by exploitation of the Clausius–Duhem inequality. In this context, the equation of heat conduction and the thermomechanical coupling is discussed regarding the diffuse interface region and the role of the latent heat due to phase evolution. Based on restrictions of the free energy, special cases of the evolution equation are presented. For a special case, the coincidence of the evolution equation obtained by the presented approach and the classical variational approach is demonstrated. Based on the presented approach, the classical Allen–Cahn/Ginzburg–Landau equation is obtained by assuming a spatially homogeneous temperature distribution.

Keywords Phase-field method · Continuum thermodynamics · Internal state variable · Heat conduction · Latent heat

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1 Introduction

1.1 Historical approach regarding nanoscale

The phase-field method (PFM) goes back to the historical works by van der Waals [1], Ginzburg and Landau [2] (cf. [3] for the English translation), Cahn and Hilliard [4], Halperin et al. [5], and Allen and Cahn [6], considering phenomena at the nano- and microscale. The method is widely used in the context of phase-transitions such as liquid–solid, liquid–liquid, solid–solid phase transitions, and, in general, the motion of singular surfaces, cf., e.g., Moelans et al. [7], Nestler and Choudhury [8], Steinbach [9]. In this context, the spatial affiliation of different phases is characterized by so-called order parameters. These order parameters can be interpreted as continuous indicator functions, which obey a nonlocal evolution equation, cf., e.g., Allen and Cahn [6, Eq. (12)], which is also referred to as kinetic equation, cf., e.g., Penrose and Fife [10, p. 45]. The derivation of the nonlocal evolution equation is variational in nature. The functional's variational derivative, which depends on the order parameters, is equilibrated by the rate of the order parameter and a positive proportionality constant, cf., e.g., Allen and Cahn [6, Eq. (11)], Penrose and Fife [10, Eq. (1.5)]. The proportionality constant might depend on the temperature and the order parameter itself, cf., e.g., Penrose and Fife [10, p. 45]. However, it has to be emphasized, that the strong form of the nonlocal evolution equation is a postulate. A different approach is considered by Penrose and Fife [10, p. 48] by accounting for an entropy functional[1] instead of a free-energy functional as the starting point for their variational derivation of the evolution of the order parameter, allowing for a temporal and spatial dependency of the temperature distribution.

1.2 Mutliphase-field method

The works by Cahn and Hilliard [4], Allen and Cahn [6] and Penrose and Fife [10] focus on the evolution of one order parameter and, thus, two phases. Moreover, the free energy densities considered by Cahn and Hilliard [4, Eq. (2.4)] and Allen and Cahn [6, Eq. (4)] do not take into account mechanical contributions and, thus, naturally do not consider mechanical phenomena. The extension of the PFM to several phases in the context of a multi-phase field method is discussed, e.g., by Steinbach et al. [12], Steinbach and Pezzolla [13], and Nestler et al. [14], Moelans et al. [7], Garcke et al. [15]. The multi-phase field method is an established method regarding the simulation of microstructure evolution and is applied to various fields, such as solidification, solid-solid phase transition, growth and coarsening of precipitations, and grain growth, cf., e.g., Moelans et al. [7], Steinbach [9], Nestler and Choudhury [8]. In this context, the focus usually lies on the micro-rather than on the nanoscale. Moreover, the consideration of, e.g., mechanical contributions is of interest and the corresponding driving forces are incorporated in the nonlocal evolution equation, e.g., [16,17].

1.3 Phase-field method from a numerical perspective

Regarding the evolution of an underlying microstructure induced by various driving forces, e.g., mechanical forces [18], the PFM is applied in the context of tracking of the evolving surfaces, cf., e.g., Chen and Khachaturyan [19], Wang et al. [20]. This interface tracking usually results in a high numerical cost if applied in a sharp interface context, cf., e.g., Chen [21]. The interpretation of the order parameter as a continuous indicator function invites us to consider the phase-field method as a numerical approximation of the sharp interface by a diffuse interface of finite thickness. The application of the PFM as a numerically efficient approximation of the sharp interface theory deviates from the original intention of the development of the PFM, in the first place. However, with this interpretation in mind, it is not necessary to resolve the physical width of the diffuse interface width but to work with an interface width appropriate for the numerical application, cf., e.g., Hohenberg and Halperin [22], Langer [23]. Moreover, since the order parameters are present as a scalar field, the tracking of the diffuse interface becomes numerically efficient, cf., e.g., Chen [21], Boettinger et al. [24], Ode et al. [25].

[1] See also the fourth footnote in Gurtin [11].

1.4 Generalization of the phase-field method

The PFM can be generalized to account for deformation and heat conduction, allowing for the consideration of coupled problems such as crack propagation [26–28], displacive phase transformations [9,29], the effect of heat conduction on microstructure evolution [30], crystal plasticity [31,32], and its application to the microstructure evolution of polycrystals [33–35]. In addition, it is also applied in the context of two-phase flows [36]. Regarding the generalization of the PFM, a more general approach than the variational approach is proposed by Gurtin [11] considering an extended principle of virtual power. His proposal is based on the continuum thermodynamical approach, which, in contrast to variational approaches, distinguishes between balance equations, representing general physical laws, and constitutive laws describing specific material behavior. Regarding the field of continuum mechanics, the discussion concerning these two approaches is well documented, cf., e.g., Truesdell and Toupin [37, pp. 594, 595], Markert [38, pp. 13, 14]. In the context of continuum mechanics, the evolution equation of the order parameter is obtained by means of an extended principle of virtual power (POVP), cf., e.g., Gurtin [11], Forest et al. [39], or by the invariance of an extended energy balance (EB) with respect to an Euclidean transformation, cf., e.g., Svendsen [40]. Both, the extended POVP and the extended EB consider the order parameter as an additional degree of freedom (DOF) of generic kind. Thus, the underlying continuum model associated with the PFM is an extended continuum.

1.5 Order parameter as internal state variable

Following the remarks of Maugin [41, p. 277] and Maugin [42, p. 80, footnote 1], in this manuscript, the order parameter is introduced as an internal state variable (ISV) and not as an additional DOF, since it can be considered as an observable but hardly controllable quantity. In addition, the following key differences support the decision to consider the order parameter as an ISV rather than an additional DOF: (i) An additional DOF can be either dissipative or non-dissipative in nature. In either case, it appears in the energy balance and, thus, contributes to the corresponding balance equations depending on its tensorial rank. On the other hand, an ISV is always of dissipative nature and consequently only appears in the dissipation inequality, cf. Maugin [42, p. 80]. (ii) In addition, an inertia is associated with an additional DOF, while an ISV does not have an inertia at all [42].

1.6 Approximation of sharp interface theory

In general, the propagating front of a phase transformation can be considered as a non-material singular surface. However, for a slowly evolving and quasi-static non-material singular surface that has no body forces acting on it, the balances of mass, linear momentum and internal energy resemble to those of a material singular surface, cf., e.g., Müller [43, Eqs. (3.31), (3.37) & (3.45)]. For this case of a sequence of quasi-equilibrium states, the work at hand provides the discussion of the PFM as an approximation of the sharp interface theory and its consistent derivation in regard of continuum thermodynamics.

1.7 Objectives of the current work

The starting point for the derivation of the PFM is the sharp interface theory, based on a Cauchy continuum containing a material singular surface. For the derivation of the PFM, the material singular surface as well as a part of the surrounding volume is replaced by a volumetric region, referred to as diffuse interface, such that the volume of the body considered in the sharp interface theory matches the volume after this replacement step. In this context, similar to the variational approaches, two free energy contributions are introduced, to account for the substitution of the singular surface by a volumetric region. In contrast to the variational approach, these two contributions are only applied to the newly introduced diffuse interface and not to the overall volume. Regarding the diffuse interface, the exploitation of the Clausius–Duhem inequality yields, among others, the nonlocal evolution equation for the order parameter, subsequently referred to as φ. For $\dot{\varphi} = 0$, the order parameter is not evolving and a diffuse equilibrium profile is obtained, cf., e.g., Cahn and Allen [44, Eq. (4)], Penrose and Fife [10, Eq. (1.2)], that can be interpreted as an approximation of the material singular surface from the sharp interface theory. In this case, the diffuse interface is free of dissipation. This also applies to a material singular surface, where the velocity field of the material singular surface and that of the continuum are identical, cf.,

e.g., Cermelli et al. [45, p. 346]. Thus, for this case, a diffuse interface theory is obtained. For $\dot{\varphi} \neq 0$, the order parameter evolves and a mobile diffuse interface is obtained. The evolution of the order parameter, which is modeled by the phase-field method, reflects the above mentioned sequence of quasi-equilibrium states, similar to the approach used in [46]. The effect of the presented approach on the heat conduction equation in the diffuse interface region is examined. This includes an intrinsically introduced latent heat contribution associated with the evolution of the order parameters. Moreover, several special cases associated with restrictions and specifications of the considered free energy are discussed. Regarding a specific case, the equivalence between the nonlocal evolution equation for the order parameter and the corresponding equation obtained through the variational approach is outlined. For simplicity, a two-phase material is considered, i.e., only one diffuse interface is considered.

1.8 Originality

Due to the assumption that the order parameter is considered as ISV and not as additional DOF, the derived phase-field method is associated with a Cauchy continuum and, thus, not an extended continuum. While, e.g., [47] also treats the order parameter as ISV, the work at hand considers a Cauchy continuum with a material singular surface as the starting point. Thus, in contrast to other approaches, e.g., [6,10,11], a diffuse interfacial region is not assumed from the outset, but introduced for approximating the material singular surface. Consequently, for the derivation of the evolution equation of the order parameter, the dissipation inequality for the singular surface is approximated instead of the dissipation inequality for the bulk material, as done in other approaches, cf., e.g., [47]. The balance equations and the constitutive behavior associated with the material singular surface are considered to hold true also in the diffuse interface. Furthermore, this work does not relate the phase-field method to the mixture theory [48,49]. In addition, this work discusses the effect of order parameters on the heat conduction equation, such as the associated latent heat, which is often neglected in the literature.

1.9 Outline

The continuum thermodynamical fundamentals of the sharp interface theory are briefly revisited in Sect. 2. Moreover, the transition to a diffuse interface is discussed and the nonlocal evolution equation for the order parameter is derived by exploiting the Clausius–Duhem inequality for the diffuse interface. In addition, the effect of the evolution of the order parameter on the heat conduction is examined. Section 3 discusses special cases that are obtained by restricting the free energy considered. Section 4 presents the equivalence between the nonlocal evolution equation of the order parameter obtained by the presented approach and the evolution equation obtained by the classical variational approach, for a special case. The manuscript is concluded in Sect. 5.

1.10 Notation

Within this manuscript, a direct tensor notation is used. In this context, first and second order tensors are denoted by lowercase and uppercase bold letters, respectively, e.g., $\boldsymbol{a}$ and $\boldsymbol{A}$. The scalar product between two vectors is written as $\boldsymbol{a} \cdot \boldsymbol{b}$, between two second order tensors as $\boldsymbol{A} \cdot \boldsymbol{B}$. While the dyadic product between two vectors is written as $\boldsymbol{a} \otimes \boldsymbol{b}$, the composition of two second order tensors is given by $\boldsymbol{A}\boldsymbol{B}$. For a given quantity $\boldsymbol{\alpha}$ of arbitrary tensorial order, its material time derivative is given by $\dot{\boldsymbol{\alpha}}$.

2 Continuum thermodynamics of sharp and diffuse interface theory

2.1 Sharp interface theory of a Cauchy continuum with a material singular surface

2.1.1 A material volume divided by a material singular surface

A material volume $\mathcal{V}$, separated by a material singular surface $\mathcal{S}$ into two subvolumes $\mathcal{V}^+$ and $\mathcal{V}^-$, is illustrated by Fig. 1. The surfaces $\mathcal{F}^+$ and $\mathcal{F}^-$ bound the two subvolumes $\mathcal{V}^+$ and $\mathcal{V}^-$, respectively, towards the

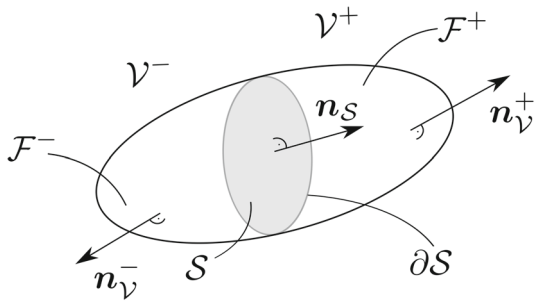

Fig. 1 Material volume, separated by a material singular surface $\mathcal{S}$ into the two subvolumes $\mathcal{V}^+$ and $\mathcal{V}^-$ that are bounded towards the surrounding by $\mathcal{F}^+$ and $\mathcal{F}^-$, cf. also [43,50]. The corresponding outer normal vectors are referred to as $\boldsymbol{n}_{\mathcal{V}}^+$ and $\boldsymbol{n}_{\mathcal{V}}^-$, respectively, while the normal of the material singular surface is denoted as $\boldsymbol{n}_{\mathcal{S}}$

surrounding. The normal vector of the singular surface is referred to as $\boldsymbol{n}_{\mathcal{S}}$, pointing from $\mathcal{V}^-$ to $\mathcal{V}^+$, while the outer normal vectors of the surfaces $\mathcal{F}^+$ and $\mathcal{F}^-$ are referred to as $\boldsymbol{n}_{\mathcal{V}}^+$ and $\boldsymbol{n}_{\mathcal{V}}^-$, respectively. Regarding the normal vectors, $\boldsymbol{n}_{\mathcal{S}} = \boldsymbol{n}_{\mathcal{V}}^+ = -\boldsymbol{n}_{\mathcal{V}}^-$ holds true as a consequence of the pill-box theorem, cf. [43]. The jump of an arbitrary quantity a across the singular surface $\mathcal{S}$ is defined as $\left[\!\left[a\right]\!\right] = a^+ - a^-$, cf., e.g., Truesdell and Toupin [37, p. 492]. Here, a^+ and a^- refer to the right- and left-hand limit of a, respectively.

2.1.2 Energy balance

The balance of total energy is given, with respect to the current configuration $\mathcal{C}$ of a material volume, by

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{V}^+\cup\mathcal{V}^-} \rho\left(e+\frac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)\,\mathrm{d}v + \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{S}} \rho_{\mathcal{S}}\left(e_{\mathcal{S}}+\frac{1}{2}\boldsymbol{v}^{\mathcal{S}}\cdot\boldsymbol{v}^{\mathcal{S}}\right)\,\mathrm{d}a \\
&= \int\limits_{\mathcal{V}^+\cup\mathcal{V}^-} \rho\left(\boldsymbol{b}\cdot\boldsymbol{v}+r\right)\,\mathrm{d}v + \int\limits_{\mathcal{F}^+\cup\mathcal{F}^-} \left(\boldsymbol{t}\cdot\boldsymbol{v}+h\right)\,\mathrm{d}a + \int\limits_{\mathcal{S}} \rho_{\mathcal{S}}\left(\boldsymbol{b}^{\mathcal{S}}\cdot\boldsymbol{v}^{\mathcal{S}}+r_{\mathcal{S}}\right)\,\mathrm{d}a.
\end{aligned} \tag{1}$$

Here, ρ and $\rho_{\mathcal{S}}$ denote the mass densities with respect to $\mathcal{V}^+\cup\mathcal{V}^-$ and $\mathcal{S}$, respectively. The specific internal energy with respect to the bulk material and the singular surface is referred to as e and $e_{\mathcal{S}}$, respectively. While $\boldsymbol{v}$ denotes the spatial velocity field of the body, $\boldsymbol{v}^{\mathcal{S}}$ denotes the velocity field of the singular surface $\mathcal{S}$. Since a material singular surface is considered, $\boldsymbol{v}^{\mathcal{S}} = \boldsymbol{v}$ and $\left[\!\left[\boldsymbol{v}\right]\!\right] = \boldsymbol{0}$ hold true [45, pp. 345, 346]. The specific body force regarding the bulk material as well as the singular surface is denoted as $\boldsymbol{b}$ and $\boldsymbol{b}^{\mathcal{S}}$, respectively. Moreover, $\boldsymbol{t}$ denotes the surface traction. The specific energy supply with respect to the bulk material is referred to as r, while $r_{\mathcal{S}}$ is referred to as the specific energy supply with respect to the singular surface. Finally, h denotes the heat flux. The balances of mass, linear and angular momentum, and internal energy for regular points

$$\dot{\rho}+\rho\mathrm{div}\left(\boldsymbol{v}\right)=0,\quad \rho\left(\boldsymbol{a}-\boldsymbol{b}\right)=\mathrm{div}\left(\boldsymbol{\sigma}\right),\quad \boldsymbol{\sigma}=\boldsymbol{\sigma}^{\mathsf{T}},\quad \rho\dot{e}=\boldsymbol{\sigma}\cdot\boldsymbol{D}+\rho r-\mathrm{div}\left(\boldsymbol{q}\right), \tag{2}$$

as well as the balances of mass, linear momentum, and internal energy for singular points

$$\dot{\rho}_{\mathcal{S}}+\rho_{\mathcal{S}}\,\mathrm{div}_{\mathrm{S}}\left(\boldsymbol{v}\right)=0,\quad \rho_{\mathcal{S}}\boldsymbol{a}-\rho_{\mathcal{S}}\boldsymbol{b}^{\mathcal{S}}=\left[\!\left[\boldsymbol{t}\right]\!\right],\quad \rho_{\mathcal{S}}\dot{e}_{\mathcal{S}}=\rho_{\mathcal{S}}r_{\mathcal{S}}-\left[\!\left[\boldsymbol{q}\right]\!\right]\cdot\boldsymbol{n}_{\mathcal{S}}, \tag{3}$$

and the existence of the Cauchy stress tensor $\boldsymbol{\sigma}$ and the heat flux vector $\boldsymbol{q}$

$$\boldsymbol{\sigma}\boldsymbol{n}_{\mathcal{V}}=\boldsymbol{t},\quad \boldsymbol{q}\cdot\boldsymbol{n}_{\mathcal{V}}=-h \tag{4}$$

can be derived by exploiting the invariance of the energy balance according to Eq. (1) with respect to a change of observer. A detailed derivation is provided, e.g., by [51,52] with respect to regular points and, e.g., by [50] with respect to singular points. Regarding Eq. (2), $\boldsymbol{a}=\dot{\boldsymbol{v}}$ denotes the acceleration and $\boldsymbol{D}$ the symmetric part of the velocity gradient. Furthermore, in Eq. (3), $\mathrm{div}_{\mathrm{S}}\left(\right)$ represents the surface divergence, cf., e.g., Cermelli et al. [45, p. 346]. Subsequently, the following assumptions are considered

A1 A small strain framework is considered. In this context, the mass density is considered to be constant, cf. Maugin [41, p. 31]. In addition, $\boldsymbol{D} = \dot{\boldsymbol{\varepsilon}}$ is considered and the partial time derivative $\partial/\partial t$ replaces the material time derivative $(\dot{\ })$, cf. Maugin [41, p. 32]. The small strain framework is also referred to as small-pertubation hypothesis, cf. Maugin [41, pp. 30–32].
A2 The quasi-static special case is considered, i.e. $\boldsymbol{a} = \boldsymbol{0}$ holds true.
A3 Body forces with respect to both regular and singular points are neglected, i.e. $\boldsymbol{b} = \boldsymbol{0}$ and $\boldsymbol{b}^{\mathcal{S}} = \boldsymbol{0}$ hold true.

2.1.3 Entropy balance

For the subsequent considerations, the global form of the entropy balance in its standard form is considered, reading

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{V}^+\cup\mathcal{V}^-} \rho\eta \,\mathrm{d}v + \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{S}} \rho_{\mathcal{S}}\eta_{\mathcal{S}} \,\mathrm{d}a \\ &\quad = -\int\limits_{\mathcal{F}^+\cup\mathcal{F}^-} \boldsymbol{\phi}^{\eta}_{\mathcal{V}}\cdot\boldsymbol{n}_{\mathcal{V}} \,\mathrm{d}a + \int\limits_{\mathcal{V}^+\cup\mathcal{V}^-} \rho\, p^{\eta}_{\mathcal{V}} + s^{\eta}_{\mathcal{V}} \,\mathrm{d}v + \int\limits_{\mathcal{S}} \rho_{\mathcal{S}}\, p^{\eta}_{\mathcal{S}} + s^{\eta}_{\mathcal{S}} \,\mathrm{d}a, \end{aligned} \tag{5}$$

cf., e.g., Müller [43]. Here, the specific entropy considering the bulk material is denoted by η, while the specific entropy with respect to the singular surface is indicated by $\eta_{\mathcal{S}}$. Moreover, regarding the bulk material and the singular surface, $p^{\eta}_{\mathcal{V}}$ and $p^{\eta}_{\mathcal{S}}$ are referred to as the specific entropy production, while $s^{\eta}_{\mathcal{V}}$ and $s^{\eta}_{\mathcal{S}}$ denote the corresponding specific entropy supply. The transport theorems, that account for a material singular surface, cf., e.g., Prahs and Böhlke [50, Eqs. (38) & (39)], the divergence theorem, cf., e.g., Gurtin et al. [53, p. 215], and the balance of mass in regular and singular points, cf. Eqs. (2) and (3), are applied to the entropy balance given by Eq. (5). To emphasize the possibility of a different material behavior in $\mathcal{V}^+$ and $\mathcal{V}^-$, the integral domain $\mathcal{V}^+\cup\mathcal{V}^-$ is separated into $\mathcal{V}^+$ and $\mathcal{V}^-$. Thus, Eq. (5) reads

$$\begin{aligned} &\int\limits_{\mathcal{V}^+} \rho_+\dot{\eta}^+ + \operatorname{div}\left(\boldsymbol{\phi}^{\eta}_{\mathcal{V}^+}\right) - s^{\eta}_{\mathcal{V}^+} \,\mathrm{d}v + \int\limits_{\mathcal{V}^-} \rho_-\dot{\eta}^- + \operatorname{div}\left(\boldsymbol{\phi}^{\eta}_{\mathcal{V}^-}\right) - s^{\eta}_{\mathcal{V}^-} \,\mathrm{d}v \\ &\quad + \int\limits_{\mathcal{S}} \rho_{\mathcal{S}}\dot{\eta}_{\mathcal{S}} + \left[\boldsymbol{\phi}^{\eta}_{\mathcal{V}}\right]\cdot\boldsymbol{n}_{\mathcal{S}} - s^{\eta}_{\mathcal{S}} \,\mathrm{d}a = \Gamma, \end{aligned} \tag{6}$$

where the global entropy production Γ is defined as

$$\Gamma := \int\limits_{\mathcal{V}^+} \rho\, p^{\eta+}_{\mathcal{V}} \,\mathrm{d}v + \int\limits_{\mathcal{V}^-} \rho\, p^{\eta-}_{\mathcal{V}} \,\mathrm{d}v + \int\limits_{\mathcal{S}} \rho_{\mathcal{S}}\, p^{\eta}_{\mathcal{S}} \,\mathrm{d}a \geq 0. \tag{7}$$

2.1.4 Constitutive assumptions

Following classical continuum thermodynamics, the subsequent assumptions are considered:

A4 The entropy fluxes are given by $\boldsymbol{\phi}_{\mathcal{V}^+} = \boldsymbol{q}^+/\theta$ and $\boldsymbol{\phi}_{\mathcal{V}^-} = \boldsymbol{q}^-/\theta$.
A5 The entropy supplies in regular points are given by $s_{\mathcal{V}^+} = \rho_+ r^+/\theta$ and $s_{\mathcal{V}^-} = \rho_- r^-/\theta$.
A6 The entropy supply in singular points is given by $s^{\eta}_{\mathcal{S}} = \rho_{\mathcal{S}} r_{\mathcal{S}}/\theta$.

In this context, the temperature is considered to be continuous across the singular surface, cf., e.g., Müller [43, p. 11]. The Assumptions A4–A6 apply for many materials and considered phenomena. But, as already pointed out by Bridgman [54, p. 146], a modification of A4 has to be considered, regarding more advanced material models, e.g., if diffusion is taken into account, cf., e.g., the comment by Maugin [42, p. 81] and the entropy flux used by Forest et al. [39, p. 80]. A modification of A4 is also necessary in the context of mixtures. Further, taking into account the Legendre-transformation, given by $\psi = e - \theta\eta$, e.g., [55] and $\psi_{\mathcal{S}} = e_{\mathcal{S}} - \theta\eta_{\mathcal{S}}$, e.g., [50], as

well as the balance of internal energy regarding regular points and singular points, cf. Eqs. (2) and (3), Eq. (6) reads

$$\begin{aligned}\Gamma = &\int_{\mathcal{V}^+} \frac{\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+}{\theta} - \frac{\operatorname{div}\left(\boldsymbol{q}^+\right)}{\theta} - \rho_+ \frac{\dot{\theta}}{\theta}\eta^+ - \rho_+ \frac{\dot{\psi}^+}{\theta} + \operatorname{div}\left(\frac{\boldsymbol{q}^+}{\theta}\right) \mathrm{d}v \\ &+ \int_{\mathcal{V}^-} \frac{\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^-}{\theta} - \frac{\operatorname{div}\left(\boldsymbol{q}^-\right)}{\theta} - \rho_- \frac{\dot{\theta}}{\theta}\eta^- - \rho_- \frac{\dot{\psi}^-}{\theta} + \operatorname{div}\left(\frac{\boldsymbol{q}^-}{\theta}\right) \mathrm{d}v \\ &+ \int_{\mathcal{S}} -\rho_{\mathcal{S}} \frac{\dot{\theta}}{\theta}\eta_{\mathcal{S}} - \rho_{\mathcal{S}} \frac{\dot{\psi}_{\mathcal{S}}}{\theta} \,\mathrm{d}a \geq 0. \end{aligned} \tag{8}$$

Here, $\psi_{\mathcal{S}}$ and $\eta_{\mathcal{S}}$ denote the specific free energy and the specific entropy of the singular surface. In the Appendix, the exploitation of Eq. (8) is carried out for completeness, see Eqs. (A.1)–(A.17) of the Appendix, yielding the potential relations for the Cauchy stress and the entropy

$$\boldsymbol{\sigma}^{\pm} = \rho_{\pm} \frac{\partial \psi^{\pm}}{\partial \boldsymbol{\varepsilon}^{\pm}}, \quad \eta^{\pm} = -\frac{\partial \psi^{\pm}}{\partial \theta}, \quad \eta_{\mathcal{S}} = -\frac{\partial \psi_{\mathcal{S}}}{\partial \theta}. \tag{9}$$

Since a Cauchy continuum with a material singular surface is considered, $\psi_{\mathcal{S}}$ can only depend on the temperature, cf. Eq. (A.15) of the Appendix. To account for the anisotropy of the underlying microstructure, e.g., in the context of slip system orientation and grain boundary orientations, an extended continuum has to be considered, e.g., [50,56].

2.2 Diffuse interface theory as approximation of the sharp interface

2.2.1 Sketch of the idea

In classical continuum mechanics, the transition between two adjacent regions with different microstructural properties is often modeled as a material singular surface, cf., e.g., grain boundaries or phase boundaries. If an evolving microstructure is considered, the propagating front of phase transformation can generally be considered as a non-material singular surface. The tracking of these sharp interfaces is both challenging and numerically costly. The phase-field method provides a numerically advantageous method for the treatment of evolving surfaces of complex interface geometry, cf., e.g., Moelans et al. [7, p. 270]. Regarding a slowly evolving, quasi-static non-material singular surface with no body forces acting on it, the balances of mass, linear momentum and internal energy are formally similar to those of a material singular surface. Thus, for this special case, the phase-field method is considered as an approximation of the sharp interface theory in the context of an evolving microstructure, in the work at hand. Here, the derivation of the phase-field method is based on the approximation of the entropy production inequality stated by Eq. (8), for the case of an evolving microstructure with migrating boundaries. In this context, the surface integral over $\mathcal{S}$ is replaced by a volume integral over $\delta\mathcal{S}$, representing the interface as a diffuse, volumetric region, cf., e.g., Moelans et al. [7], illustrated by Fig. 2. Moreover, the volume integrals over $\mathcal{V}^+$ and $\mathcal{V}^-$ are replaced by volume integrals over the smaller volumes $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$, such that

$$\mathcal{V}^+ \cup \mathcal{V}^- = \tilde{\mathcal{V}}^+ \cup \tilde{\mathcal{V}}^- \cup \delta\mathcal{S} \tag{10}$$

holds true. The main concept is that the diffuse interface is described by an ISV φ, which is referred to as order parameter. In contrast to an additional internal DOF, the ISV does not enter the energy balance, cf. Maugin [42, p. 80], and, thus, does not affect the balance equations obtained by invariance considerations of the energy balance and stated by Eqs. (2) and (3). The replacement of the surface integral over $\mathcal{S}$ is accompanied by accounting for additional energy contributions that depend on the order parameter φ and its gradient. It is emphasized that the work at hand does not discuss the choice of these contributions, nor the effect of different formulations of the contributions on solutions of boundary value problems. A detailed discussion on the choice of the specific contributions and the effect on the phase evolution is provided by [57]. Here, the additional contributions are taken into account in general without using a specific formulation. However, to interpret the diffuse interface as an approximation of the sharp interface, it must have a finite thickness. This requirement

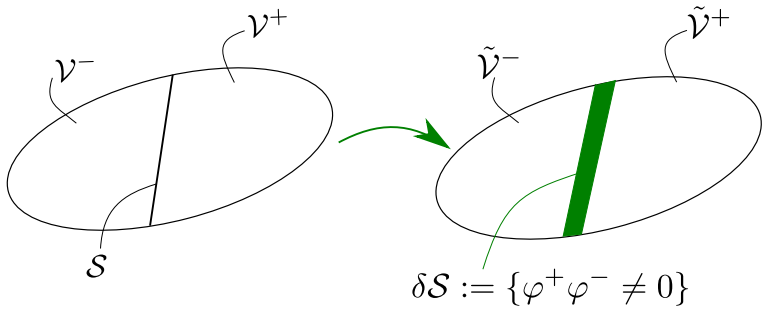

Fig. 2 Illustration of the transition from the sharp interface to the diffuse interface. The material singular surface $\mathcal{S}$ and portions of the adjacent volumes $\mathcal{V}^+$ and $\mathcal{V}^-$ are replaced by a volume $\delta\mathcal{S}$, representing the interface as a diffuse, volumetric region. In this context, the volumes $\mathcal{V}^+$ and $\mathcal{V}^-$ are replaced with the smaller volumes $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$, respectively, i.e., $\mathcal{V}^+ \cup \mathcal{V}^- = \tilde{\mathcal{V}}^+ \cup \tilde{\mathcal{V}}^- \cup \delta\mathcal{S}$ holds true. The order parameters identify the corresponding volume: Within $\tilde{\mathcal{V}}^+$, $\varphi^+ = 1$ and $\varphi^- = 0$ hold true, while within $\tilde{\mathcal{V}}^-$, $\varphi^- = 1$ and $\varphi^+ = 0$ are valid. Within the diffuse interface, illustrated by the green domain, the product of the order parameters does not vanish, while outside the diffuse interface, $\varphi^+\varphi^- = 0$ holds true

may not be met if the additional energy contributions are unsuitably chosen. This work aims at the derivation of the evolution equation of the ISV φ by the exploitation of the approximated dissipation inequality. The idea is inspired by the procedure used by, e.g., [47,58], and other authors. However, in this work, the specific free energy of the diffuse interface accounts for an interpolation of the specific free energy contributions that are associated with the bulk regions of the sharp interface theory. This allows a direct comparison of the governing equations between the sharp and diffuse interface theory. Moreover, it motivates to account for constitutive restrictions related to the sharp interface. In the work at hand, the balance equations for the singular surface, cf. Eq. (3), as well as the potential relations given by Eq. (9) are considered to hold true in each point of the diffuse interface region. In contrast and as extension to [58], this manuscript's considerations are not limited to isothermal behavior. Furthermore, in contrast to [47], the approximation of the entropy production inequality of the singular surface is considered for the derivation of the evolution equation of the order parameter instead of the entropy production inequality of the bulk material.

2.2.2 Approximation of entropy production inequality

The global entropy production Γ of the sharp interface theory is approximated by $\tilde{\Gamma}$, such that

$$\tilde{\Gamma} \approx \Gamma, \quad \tilde{\Gamma} \geq 0 \tag{11}$$

holds, with $\tilde{\Gamma}$ according to the following ansatz

$$\tilde{\Gamma} = \tilde{\Gamma}_{\tilde{\mathcal{V}}^+} + \tilde{\Gamma}_{\tilde{\mathcal{V}}^-} + \tilde{\Gamma}_{\delta\mathcal{S}} \geq 0, \tag{12}$$

$$\tilde{\Gamma}_{\tilde{\mathcal{V}}^+} = \int_{\tilde{\mathcal{V}}^+} \frac{\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+}{\theta} - \frac{\operatorname{div}\left(\boldsymbol{q}^+\right)}{\theta} - \rho_+ \frac{\dot{\theta}}{\theta}\eta^+ - \rho_+ \frac{\dot{\psi}^+}{\theta} + \operatorname{div}\left(\frac{\boldsymbol{q}^+}{\theta}\right) \mathrm{d}v, \tag{13}$$

$$\tilde{\Gamma}_{\tilde{\mathcal{V}}^-} = \int_{\tilde{\mathcal{V}}^-} \frac{\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^-}{\theta} - \frac{\operatorname{div}\left(\boldsymbol{q}^-\right)}{\theta} - \rho_- \frac{\dot{\theta}}{\theta}\eta^- - \rho_- \frac{\dot{\psi}^-}{\theta} + \operatorname{div}\left(\frac{\boldsymbol{q}^-}{\theta}\right) \mathrm{d}v, \tag{14}$$

$$\tilde{\Gamma}_{\delta\mathcal{S}} = \int_{\delta\mathcal{S}} -\rho_{\mathcal{S}} \frac{\dot{\theta}}{\theta}\tilde{\eta}_{\mathcal{S}} - \rho_{\mathcal{S}} \frac{\dot{\tilde{\psi}}_{\mathcal{S}}}{\theta} \mathrm{d}v. \tag{15}$$

The contributions $\tilde{\psi}_{\mathcal{S}}$ and $\tilde{\eta}_{\mathcal{S}}$ are normalized by the mass density $\rho_{\mathcal{S}}$ associated with the sharp singular surface, truncating $\rho_{\mathcal{S}}$ from Eq. (15) in the context of small deformations, reading

$$\tilde{\psi}_{\mathcal{S}} = \frac{h(\varphi)\rho_+ + \overline{h}(\varphi)\rho_-}{\rho_{\mathcal{S}}}\psi_{\mathcal{S}}\left(\psi_{\text{grad}} + \psi_{\text{pot}}\right) + \frac{1}{\rho_{\mathcal{S}}}\left(h(\varphi)\rho_+\psi^+ + \overline{h}(\varphi)\rho_-\psi^-\right) \tag{16}$$

$$\tilde{\eta}_{\mathcal{S}} = -\frac{\partial\tilde{\psi}_{\mathcal{S}}}{\partial\theta} = \frac{h(\varphi)\rho_+ + \overline{h}(\varphi)\rho_-}{\rho_{\mathcal{S}}}\eta_{\mathcal{S}}\left(\psi_{\text{grad}} + \psi_{\text{pot}}\right) + \frac{1}{\rho_{\mathcal{S}}}\left(h(\varphi)\rho_+\eta^+ + \overline{h}(\varphi)\rho_-\eta^-\right). \tag{17}$$

The last two contributions of Eq. (16) illustrate that the ansatz for $\tilde{\psi}_{\mathcal{S}}$ interpolates the free energy densities f^+ and f^- such that

$$\overline{f}_{\mathcal{V}} = h(\varphi)f^+ + \overline{h}(\varphi)f^- = h(\varphi)\rho_+\psi^+ + \overline{h}(\varphi)\rho_-\psi^- = \overline{\rho\psi} \tag{18}$$

holds true, with $\overline{f}_{\mathcal{V}}$ denoting the free energy density of the bulk material within $\delta\mathcal{S}$. It is pointed out that the interpolation functions $h(\varphi)$ and $\overline{h}(\varphi)$, the contributions ψ_{pot} and ψ_{grad}, and the mass densities ρ_+, ρ_-, and $\rho_{\mathcal{S}}$ do not depend on the temperature. Thus, $\tilde{\eta}_{\mathcal{S}}$ follows from the potential relations according to Eqs. $(9)_2$ and $(9)_3$. In this context, the densities ρ_+ and ρ_-, as well as the specific free energies ψ^+, ψ^-, and the specific entropies η^+, and η^- are the same as in the theory of sharp interfaces. The contributions ψ_{grad} and ψ_{pot} are due to the approximation of the sharp interface and referred to as gradient and potential contribution. A discussion on the nature of these two contributions in the context of the approximation of the singular surface towards the diffuse interface is provided, e.g., by Moelans et al. [7, pp. 273, 274]. Subsequently, the following assumption is considered:

A7 While the gradient contribution ψ_{grad} depends on the order parameter φ and its gradient $\nabla\varphi$, the potential contribution ψ_{pot} only depends on the order parameter φ, i.e.,

$$\psi_{\text{grad}} = \psi_{\text{grad}}(\varphi, \nabla\varphi), \quad \psi_{\text{pot}} = \psi_{\text{pot}}(\varphi) \tag{19}$$

holds true, cf., e.g., Nestler et al. [14, p. 2].

While it is possible to use $h(\varphi) = \varphi$ as an interpolation function, this work does not provide any further specification of the interpolation functions $h(\varphi)$ and $\overline{h}(\varphi)$. In general, different interpolation functions can be used as pointed out, e.g., by Nestler et al. [14, p. 2], Moelans [59]. This leads to some ambiguity regarding the subsequently derived, governing equations. It has to be stressed that this ambiguity is present due to the possibility to choose from different interpolation functions, which is common in the PFM, and not inherent to the approach presented. Regarding the interpolation functions $h(\varphi)$ and $\overline{h}(\varphi)$, the following properties have to be fulfilled

$$\overline{h}(\varphi) = 1 - h(\varphi), \quad \frac{\partial\overline{h}(\varphi)}{\partial\varphi} = -\frac{\partial h(\varphi)}{\partial\varphi}, \tag{20}$$

cf., e.g., Schneider et al. [60, p. 210]. Moreover, the choice and limitations of the interpolation functions $h(\varphi)$ and $\overline{h}(\varphi)$ are discussed by Moelans [59, pp. 1077, 1078]. Subsequently, the following assumption is considered:

A8 The approximated entropy production inequality according to Eq. (12) is fulfilled, if each integral is non-negative. Thus, it is required that

$$\tilde{\Gamma}_{\tilde{\mathcal{V}}^+} \geq 0, \quad \tilde{\Gamma}_{\tilde{\mathcal{V}}^-} \geq 0, \quad \tilde{\Gamma}_{\delta\mathcal{S}} \geq 0 \tag{21}$$

are satisfied, which is fulfilled if each integrand is non-negative.

This requirement yields three inequalities that are discussed in the next subsections.

2.2.3 Remark on the dissipation in $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$

Multiplication of the integrands of Eqs. $(21)_1$ and $(21)_2$ with the temperature yields the Clausius–Duhem inequality, cf. Eq. (A.3) in the Appendix, for $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$, respectively. Thus, Assumptions A18, A19, and A20, stated in the Appendix, are adopted subsequently, and the results according to Eqs. (A.10) and (A.12) of the Appendix are adopted for $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$, subsequently.

2.2.4 Dissipation in the diffuse interface

Taking into account Eqs. (16) and (17), the integrand of the Eq. (15) with respect to $\delta\mathcal{S}$, subsequently referred to as $\mathcal{L}_\mathcal{S}$, can be written as

$$\begin{aligned}\mathcal{L}_\mathcal{S} = -\rho_\mathcal{S}\frac{\dot{\theta}}{\theta}\tilde{\eta}_\mathcal{S} - \frac{\rho_\mathcal{S}}{\theta}\Bigg(&\frac{h(\varphi)\rho_+ + \overline{h}(\varphi)\rho_-}{\rho_\mathcal{S}}\psi_\mathcal{S}\left(\psi_{\text{grad}} + \psi_{\text{pot}}\right)\\ &+h(\varphi)\frac{\rho_+}{\rho_\mathcal{S}}\psi^+ + \overline{h}(\varphi)\frac{\rho_-}{\rho_\mathcal{S}}\psi^-\Bigg)^{\cdot}, \quad \mathcal{L}_\mathcal{S} \geq 0.\end{aligned} \tag{22}$$

The inequality according to Eq. $(22)_2$ represents the Clausius–Duhem inequality for points in $\delta\mathcal{S}$. Since small deformations are considered according to A1, $\dot{\rho}_+ = 0, \quad \dot{\rho}_- = 0, \quad \dot{\rho}_\mathcal{S} = 0$ holds true. Accounting for this, Eq. (22) reads

$$\begin{aligned}\mathcal{L}_\mathcal{S} = &-\rho_\mathcal{S}\frac{\dot{\theta}}{\theta}\tilde{\eta}_\mathcal{S} - \frac{1}{\theta}\Bigg\{\left(\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi}\rho_+ + \frac{\partial\overline{h}(\varphi)}{\partial\varphi}\dot{\varphi}\rho_-\right)\psi_\mathcal{S}\left(\psi_{\text{grad}} + \psi_{\text{pot}}\right)\\ &+\left(h(\varphi)\rho_+ + \overline{h}(\varphi)\rho_-\right)\left(\dot{\psi}_\mathcal{S}\left(\psi_{\text{grad}} + \psi_{\text{pot}}\right) + \psi_\mathcal{S}\left(\dot{\psi}_{\text{grad}} + \dot{\psi}_{\text{pot}}\right)\right)\\ &+\left(\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi}\rho_+\psi^+ + \frac{\partial\overline{h}(\varphi)}{\partial\varphi}\dot{\varphi}\rho_-\psi^-\right) + h(\varphi)\rho_+\dot{\psi}^+ + \overline{h}(\varphi)\rho_-\dot{\psi}^-\Bigg\}\end{aligned} \tag{23}$$

Taking into account Eq. (A.17) as well as Eq. (17), and introducing

$$\tilde{\eta}^*_\mathcal{S} = h(\varphi)\frac{\rho_+}{\rho_\mathcal{S}}\eta^+ + \overline{h}(\varphi)\frac{\rho_-}{\rho_\mathcal{S}}\eta^-, \tag{24}$$

Equation (23) can be written as

$$\begin{aligned}\mathcal{L}_\mathcal{S} = &-\rho_\mathcal{S}\frac{\dot{\theta}}{\theta}\tilde{\eta}^*_\mathcal{S} - \frac{1}{\theta}\Bigg\{\left(\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi}\rho_+ + \frac{\partial\overline{h}(\varphi)}{\partial\varphi}\dot{\varphi}\rho_-\right)\psi_\mathcal{S}\left(\psi_{\text{grad}} + \psi_{\text{pot}}\right)\\ &+\left(h(\varphi)\rho_+ + \overline{h}(\varphi)\rho_-\right)\psi_\mathcal{S}\left(\dot{\psi}_{\text{grad}} + \dot{\psi}_{\text{pot}}\right)\\ &+\left(\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi}\rho_+\psi^+ + \frac{\partial\overline{h}(\varphi)}{\partial\varphi}\dot{\varphi}\rho_-\psi^-\right) + h(\varphi)\rho_+\dot{\psi}^+ + \overline{h}(\varphi)\rho_-\dot{\psi}^-\Bigg\}\end{aligned} \tag{25}$$

Introducing $\boldsymbol{\xi} = \partial\psi_{\text{grad}}/\partial\nabla\varphi$ and taking into account A7 as well as Eqs. (20) and (25) reads after multiplication with θ

$$\begin{aligned}\theta\mathcal{L}_\mathcal{S} = &-\rho_\mathcal{S}\dot{\theta}\tilde{\eta}^*_\mathcal{S} - \Bigg\{\left(\rho_+ - \rho_-\right)\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi}\,\psi_\mathcal{S}\left(\psi_{\text{grad}} + \psi_{\text{pot}}\right)\\ &+\left(h(\varphi)\rho_+ + (1-h(\varphi))\rho_-\right)\psi_\mathcal{S}\left(\frac{\partial\psi_{\text{grad}}}{\partial\varphi}\dot{\varphi} + \boldsymbol{\xi}\cdot\nabla\dot{\varphi} + \frac{\partial\psi_{\text{pot}}}{\partial\varphi}\dot{\varphi}\right)\\ &+\left(\rho_+\psi^+ - \rho_-\psi^-\right)\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi} + h(\varphi)\rho_+\dot{\psi}^+ + (1-h(\varphi))\rho_-\dot{\psi}^-\Bigg\}.\end{aligned} \tag{26}$$

Inserting Eq. (26) in Eq. $(22)_2$, application of the product rule as well as of the divergence theorem for a continuum without a singular surface yields

$$\begin{aligned}
\int_{\delta\mathcal{S}} & -\rho_{\mathcal{S}}\dot{\theta}\tilde{\eta}^{*}_{\mathcal{S}} - \Big\{(\rho_{+}-\rho_{-})\,\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi}\,\psi_{\mathcal{S}}\left(\psi_{\text{grad}}+\psi_{\text{pot}}\right) \\
& + (h(\varphi)\rho_{+}+(1-h(\varphi))\rho_{-})\,\psi_{\mathcal{S}}\left(\frac{\partial\psi_{\text{grad}}}{\partial\varphi}\dot{\varphi}+\frac{\partial\psi_{\text{pot}}}{\partial\varphi}\dot{\varphi}\right) - \operatorname{div}(\boldsymbol{\Xi})\,\dot{\varphi} \\
& + \left(\rho_{+}\psi^{+}-\rho_{-}\psi^{-}\right)\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi} + h(\varphi)\rho_{+}\dot{\psi}^{+} + (1-h(\varphi))\rho_{-}\dot{\psi}^{-}\Big\}\,\mathrm{d}v \\
& - \int_{\partial\delta\mathcal{S}}\left(\boldsymbol{\Xi}\cdot\boldsymbol{n}^{\delta\mathcal{S}}_{\mathcal{V}}\right)\dot{\varphi}\,\mathrm{d}a \geq 0, \quad \boldsymbol{\Xi} = (h(\varphi)\rho_{+}+(1-h(\varphi))\rho_{-})\,\psi_{\mathcal{S}}\,\boldsymbol{\xi}
\end{aligned} \tag{27}$$

with $\boldsymbol{n}^{\delta\mathcal{S}}_{\mathcal{V}}$ denoting the normal of $\delta\mathcal{S}$ on $\partial\delta\mathcal{S}$. Dividing the boundary of $\partial\delta\mathcal{S}$ into a Neumann section $\partial\delta\mathcal{S}_N$ and a Dirichlet section of rate type $\partial\delta\mathcal{S}_D$, the non-negativity of inequality (27) with respect to $\partial\delta\mathcal{S}$ can be fulfilled by the following boundary conditions

$$\boldsymbol{\Xi}\cdot\boldsymbol{n}^{\delta\mathcal{S}}_{\mathcal{V}} = 0 \quad \rightsquigarrow \quad \boldsymbol{\xi}\cdot\boldsymbol{n}^{\delta\mathcal{S}}_{\mathcal{V}} = 0, \quad \forall\boldsymbol{x}\in\partial\delta\mathcal{S}_N, \quad \dot{\varphi} = 0, \quad \forall\boldsymbol{x}\in\partial\delta\mathcal{S}_D, \tag{28}$$

cf., e.g., Gladkov and Svendsen [61, Eqs. (33) & (34)], as $(h(\varphi)\rho_{+}+(1-h(\varphi))\rho_{-}) \neq 0$ holds true. It has to be pointed out that Eq. (28) has to hold on $\partial\delta\mathcal{S}$ however not on $\partial\mathcal{V}$ with $\mathcal{V} = \tilde{\mathcal{V}}^{+}\cup\tilde{\mathcal{V}}^{-}\cup\delta\mathcal{S}$. The fulfillment of the boundary condition according to Eq. (28) on $\partial\mathcal{V}$ is common if the derivation of the PFM considers a volume integral from the outset. In this context, cf., e.g., Gurtin [11, eq. (1.5)],[2] regarding the classical approach that accounts for the variational derivative, or, cf., e.g., Gurtin [11, p. 182] regarding an approach based on an extended principle of virtual power. Collecting the rates and taking into account Eqs. (28) and (27) can be written as

$$\begin{aligned}
\int_{\delta\mathcal{S}} & -\rho_{\mathcal{S}}\dot{\theta}\tilde{\eta}^{*}_{\mathcal{S}} - \Big\{\big[\rho\big]\frac{\partial h(\varphi)}{\partial\varphi}\,\psi_{\mathcal{S}}\left(\psi_{\text{grad}}+\psi_{\text{pot}}\right) \\
& + (h(\varphi)\rho_{+}+(1-h(\varphi))\rho_{-})\,\psi_{\mathcal{S}}\left(\frac{\partial\psi_{\text{grad}}}{\partial\varphi}+\frac{\partial\psi_{\text{pot}}}{\partial\varphi}\right) - \operatorname{div}(\boldsymbol{\Xi}) + \big[\rho\psi\big]\frac{\partial h(\varphi)}{\partial\varphi}\Big\}\,\dot{\varphi} \\
& - \left(h(\varphi)\rho_{+}\dot{\psi}^{+}+(1-h(\varphi))\rho_{-}\dot{\psi}^{-}\right)\mathrm{d}v \geq 0,
\end{aligned} \tag{29}$$

where $\big[\rho\big] = \rho_{+}-\rho_{-}$ and $\big[\rho\psi\big] = \rho_{+}\psi^{+}-\rho_{-}\psi^{-}$ are introduced.

2.2.5 Constitutive assumptions

Subsequently, the following assumption is considered:

A9 The dependency of the bulk contributions of the specific free energy ψ^{+} and ψ^{-} is given by

$$\psi^{+} = \psi^{+}(\boldsymbol{\varepsilon}^{+},\boldsymbol{\varepsilon}^{*+},\varphi,\boldsymbol{\alpha}^{+},\theta), \quad \psi^{-} = \psi^{-}(\boldsymbol{\varepsilon}^{-},\boldsymbol{\varepsilon}^{*-},\varphi,\boldsymbol{\alpha}^{-},\theta). \tag{30}$$

Within this section, the specific free energies are not subdivided into individual contributions. However, this is discussed in the subsequent section.

Applying the chain rule with respect to Eqs. (30) and (29) can be written as

$$\mathcal{D}^{\varphi}_{\delta\mathcal{S}} + \mathcal{D}^{\theta}_{\delta\mathcal{S}} + \mathcal{D}^{\text{mech}}_{\delta\mathcal{S}} \geq 0, \tag{31}$$

[2] Regarding Gurtin [11, eq. (1.5)] this condition is tacitly assumed to hold on $\partial\mathcal{V}$ in order to obtain Eq. $(1.5)_2$ from $(1.5)_1$.

with the contribution $\mathcal{D}^{\varphi}_{\delta\mathcal{S}}$ linear in the rate of the order parameter

$$\begin{aligned}\mathcal{D}^{\varphi}_{\delta\mathcal{S}} := \int_{\delta\mathcal{S}} -\Big\{ &\big[\rho\big]\frac{\partial h(\varphi)}{\partial\varphi}\,\psi_{\mathcal{S}}\left(\psi_{\mathrm{grad}}+\psi_{\mathrm{pot}}\right)\\ &+\left(h(\varphi)\rho_{+}+(1-h(\varphi))\rho_{-}\right)\psi_{\mathcal{S}}\left(\frac{\partial\psi_{\mathrm{grad}}}{\partial\varphi}+\frac{\partial\psi_{\mathrm{pot}}}{\partial\varphi}\right)-\mathrm{div}\left(\boldsymbol{\Xi}\right)\\ &+\big[\rho\psi\big]\frac{\partial h(\varphi)}{\partial\varphi}+h(\varphi)\rho_{+}\frac{\partial\psi^{+}}{\partial\varphi}+(1-h(\varphi))\rho_{-}\frac{\partial\psi^{-}}{\partial\varphi}\Big\}\,\dot{\varphi}\,\mathrm{d}v,\end{aligned}\tag{32}$$

the contribution $\mathcal{D}^{\theta}_{\delta\mathcal{S}}$ linear in the rate of the temperature

$$\mathcal{D}^{\theta}_{\delta\mathcal{S}}=\int_{\delta\mathcal{S}} -\left\{\rho_{\mathcal{S}}\tilde{\eta}^{*}_{\mathcal{S}}+h(\varphi)\rho_{+}\frac{\partial\psi^{+}}{\partial\theta}+(1-h(\varphi))\rho_{-}\frac{\partial\psi^{-}}{\partial\theta}\right\}\dot{\theta}\,\mathrm{d}v,\tag{33}$$

and the contribution $\mathcal{D}^{\mathrm{mech}}_{\delta\mathcal{S}}$ linear in the remaining rates

$$\begin{aligned}\mathcal{D}^{\mathrm{mech}}_{\delta\mathcal{S}} := \int_{\delta\mathcal{S}} -\Big\{ &h(\varphi)\rho_{+}\left(\frac{\partial\psi^{+}}{\partial\boldsymbol{\varepsilon}^{+}}\cdot\dot{\boldsymbol{\varepsilon}}^{+}+\frac{\partial\psi^{+}}{\partial\boldsymbol{\varepsilon}^{*+}}\cdot\dot{\boldsymbol{\varepsilon}}^{*+}+\frac{\partial\psi^{+}}{\partial\boldsymbol{\alpha}^{+}}\cdot\dot{\boldsymbol{\alpha}}^{+}\right)\\ &+(1-h(\varphi))\rho_{-}\left(\frac{\partial\psi^{-}}{\partial\boldsymbol{\varepsilon}^{-}}\cdot\dot{\boldsymbol{\varepsilon}}^{-}+\frac{\partial\psi^{-}}{\partial\boldsymbol{\varepsilon}^{*-}}\cdot\dot{\boldsymbol{\varepsilon}}^{*-}+\frac{\partial\psi^{-}}{\partial\boldsymbol{\alpha}^{-}}\cdot\dot{\boldsymbol{\alpha}}^{-}\right)\Big\}\,\mathrm{d}v.\end{aligned}\tag{34}$$

2.2.6 Decoupled dissipative contributions

For the subsequent procedure, it has to be stressed that

- $\mathcal{D}^{\varphi}_{\delta\mathcal{S}}$ does only depend on the rate $\dot{\varphi}$,
- $\mathcal{D}^{\theta}_{\delta\mathcal{S}}$ does only depend on the rate $\dot{\theta}$,
- $\mathcal{D}^{\mathrm{mech}}_{\delta\mathcal{S}}$ does only depend on the rates $\dot{\boldsymbol{\varepsilon}}^{+}$, $\dot{\boldsymbol{\varepsilon}}^{*+}$, $\dot{\boldsymbol{\alpha}}^{+}$, $\dot{\boldsymbol{\varepsilon}}^{-}$, $\dot{\boldsymbol{\varepsilon}}^{*-}$, and $\dot{\boldsymbol{\alpha}}^{-}$.

Thus, no coupling between $\mathcal{D}^{\varphi}_{\delta\mathcal{S}}$, $\mathcal{D}^{\theta}_{\delta\mathcal{S}}$, and $\mathcal{D}^{\mathrm{mech}}_{\delta\mathcal{S}}$ is present with respect to the rates considered. Consequently, requiring

$$\mathcal{D}^{\varphi}_{\delta\mathcal{S}}\geq 0,\quad \mathcal{D}^{\theta}_{\delta\mathcal{S}}\geq 0,\quad \mathcal{D}^{\mathrm{mech}}_{\delta\mathcal{S}}\geq 0\tag{35}$$

independently of each other is possible and fulfills the dissipation inequality given by Eq. (31).

2.2.7 Fulfillment of $\mathcal{D}^{\varphi}_{\delta\mathcal{S}}\geq 0$: evolution equation of the order parameter

The diffuse interface is a mobile, evolving interface for $\dot{\varphi}\neq 0$. Thus, additional constitutive equations, such as the evolution equation of the order parameter φ are necessary. For a nonequilibrium state, the classical PFM approach postulates that the variational derivative of the free energy function is proportional to the rate of the order parameter, cf. Allen and Cahn [6, Eq. (11)]. Here, the evolution equation for the order parameter φ is obtained by exploitation of the Clausius–Duhem inequality with respect to the diffuse interface. The condition according to Eq. $(35)_1$ can be fulfilled by a variety of different evolution equations for φ. A possible and simple choice is given by linear irreversible thermodynamics, reading

$$\begin{aligned}\dot{\varphi}=\dot{\varphi}_{0}\Big\{ &-\big[\rho\big]\frac{\partial h(\varphi)}{\partial\varphi}\,\psi_{\mathcal{S}}\left(\psi_{\mathrm{grad}}+\psi_{\mathrm{pot}}\right)-\big[\rho\psi\big]\frac{\partial h(\varphi)}{\partial\varphi}\\ &+\mathrm{div}\left(\boldsymbol{\Xi}\right)-\left(h(\varphi)\rho_{+}+(1-h(\varphi))\rho_{-}\right)\psi_{\mathcal{S}}\left(\frac{\partial\psi_{\mathrm{grad}}}{\partial\varphi}+\frac{\partial\psi_{\mathrm{pot}}}{\partial\varphi}\right)\\ &-\left(h(\varphi)\rho_{+}\frac{\partial\psi^{+}}{\partial\varphi}+(1-h(\varphi))\rho_{-}\frac{\partial\psi^{-}}{\partial\varphi}\right)\Big\},\quad \dot{\varphi}_{0}\geq 0\end{aligned}\tag{36}$$

with the referential rate $\dot{\varphi}_{0}$. It is stressed that despite its resemblance with a balance equation, Eq. (36) represents a nonlocal evolution equation of the order parameter as ISV. A detailed discussion regarding nonlocal evolution equation and balance equations is provided by [52].

2.2.8 Fulfillment of $\mathcal{D}^{\varphi}_{\delta\mathcal{S}} \geq 0$: equilibrium state of the order parameter

The classical derivation of the PFM originates from the discussion of an equilibrium state which is characterized by the vanishing variational derivative of a given (free energy) functional, cf., e.g., Allen and Cahn [6, p. 1087], Penrose and Fife [10, Eq. (1.2)]. This leads to a non-evolving equilibrium profile which can be interpreted as a material singular surface. Regarding the sharp interface theory, Eq. (A.17) of the Appendix clearly indicates that the material singular surface $\mathcal{S}$, which does not exhibit any evolution since $\boldsymbol{v}^{\mathcal{S}} = \boldsymbol{v}$ and $\left[\boldsymbol{v}\right] = \boldsymbol{0}$ holds, cf., e.g., [45, pp. 345, 346], is free of dissipation. This corresponds to a vanishing of $\mathcal{D}^{\varphi}_{\delta\mathcal{S}}$ in Eq. (32). Consequently, in case of a non-evolving diffuse interface $\delta\mathcal{S}$, no additional dissipation is introduced into the system due to $\mathcal{D}^{\varphi}_{\delta\mathcal{S}}$, compared to the sharp interface theory. Taking into account $\dot{\varphi} = 0$, Eq. (36) provides the partial differential equation (PDE) of the equilibrium state regarding the order parameter, reading

$$\begin{aligned}
&\left[\rho\right] \frac{\partial h(\varphi)}{\partial \varphi}\, \psi_{\mathcal{S}} \left(\psi_{\text{grad}} + \psi_{\text{pot}}\right) \\
&\quad + \left(h(\varphi)\rho_{+} + (1 - h(\varphi))\rho_{-}\right) \psi_{\mathcal{S}} \left(\frac{\partial \psi_{\text{grad}}}{\partial \varphi} + \frac{\partial \psi_{\text{pot}}}{\partial \varphi}\right) - \operatorname{div}\left(\boldsymbol{\Xi}\right) \\
&\quad + \left[\rho\psi\right] \frac{\partial h(\varphi)}{\partial \varphi} + h(\varphi)\rho_{+} \frac{\partial \psi^{+}}{\partial \varphi} + (1 - h(\varphi))\rho_{-} \frac{\partial \psi^{-}}{\partial \varphi} = 0.
\end{aligned} \tag{37}$$

This PDE of the equilibrium state is discussed in more detail in a subsequent section, where also the presented approach is compared with the classical PFM variational approach.

2.2.9 Fulfillment of $\mathcal{D}^{\theta}_{\delta\mathcal{S}} \geq 0$

Since the rate $\dot{\theta}$ is not arbitrary but determined by the instationary heat equation, the condition Eq. $(35)_2$ can be fulfilled by

$$\rho_{\mathcal{S}} \tilde{\eta}^{*}_{\mathcal{S}} + h(\varphi)\rho_{+} \frac{\partial \psi^{+}}{\partial \theta} + (1 - h(\varphi))\rho_{-} \frac{\partial \psi^{-}}{\partial \theta} = 0. \tag{38}$$

Accounting for Eqs. (24) and (20), Eq. (38) reads

$$h(\varphi)\rho_{+}\eta^{+} + \overline{h}(\varphi)\rho_{-}\eta^{-} + h(\varphi)\rho_{+} \frac{\partial \psi^{+}}{\partial \theta} + \overline{h}(\varphi)\rho_{-} \frac{\partial \psi^{-}}{\partial \theta} = 0. \tag{39}$$

With the generalization of Eq. $(9)_2$ to $\tilde{\mathcal{V}}^{+}$ and $\tilde{\mathcal{V}}^{-}$, Eq. (39) is given by

$$h(\varphi)\rho_{+}\eta^{+} + \overline{h}(\varphi)\rho_{-}\eta^{-} - h(\varphi)\rho_{+}\eta^{+} - \overline{h}(\varphi)\rho_{-}\eta^{-} = 0 \tag{40}$$

and, thereby, fulfills $\mathcal{D}^{\theta}_{\delta\mathcal{S}} \geq 0$. This holds true for all special cases discussed in subsequent sections.

2.2.10 Fulfillment of $\mathcal{D}^{\text{mech}}_{\delta\mathcal{S}} \geq 0$

Taking into account Eq. $(9)_1$, adapted for $\tilde{\mathcal{V}}^{+}$ as well as $\tilde{\mathcal{V}}^{-}$, i.e., $\rho_{+}\partial\psi^{+}/\partial\boldsymbol{\varepsilon}^{+} = \boldsymbol{\sigma}^{+}$ and $\rho_{-}\partial\psi^{-}/\partial\boldsymbol{\varepsilon}^{-} = \boldsymbol{\sigma}^{-}$, Eq. (34) can be written as

$$\begin{aligned}
\int_{\delta\mathcal{S}} &- h(\varphi)\rho_{+}\boldsymbol{\sigma}^{+} \cdot \dot{\boldsymbol{\varepsilon}}^{+} - (1 - h(\varphi))\rho_{-}\boldsymbol{\sigma}^{-} \cdot \dot{\boldsymbol{\varepsilon}}^{-} - \left\{ h(\varphi)\rho_{+} \left(\frac{\partial \psi^{+}}{\partial \boldsymbol{\varepsilon}^{*+}} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial \psi^{+}}{\partial \boldsymbol{\alpha}^{+}} \cdot \dot{\boldsymbol{\alpha}}^{+}\right) \right. \\
&\left. + (1 - h(\varphi))\rho_{-} \left(\frac{\partial \psi^{-}}{\partial \boldsymbol{\varepsilon}^{*-}} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial \psi^{-}}{\partial \boldsymbol{\alpha}^{-}} \cdot \dot{\boldsymbol{\alpha}}^{-}\right) \right\} \mathrm{d}v \geq 0
\end{aligned} \tag{41}$$

Accounting for the symmetry of the stress tensors $\boldsymbol{\sigma}^+$ and $\boldsymbol{\sigma}^-$, as well as for the strain rates $\dot{\boldsymbol{\varepsilon}}^+ = \operatorname{sym}(\operatorname{grad}(\dot{\boldsymbol{u}}_+))$ and $\dot{\boldsymbol{\varepsilon}}^- = \operatorname{sym}(\operatorname{grad}(\dot{\boldsymbol{u}}_-))$, with $\dot{\boldsymbol{u}}_+$ and $\dot{\boldsymbol{u}}_-$ denoting the material time derivatives of the phase-specific displacement fields $\boldsymbol{u}_+$ and $\boldsymbol{u}_-$, application of the product rule leads to

$$\begin{aligned}
\int_{\delta\mathcal{S}} & -\operatorname{div}\left(h(\varphi)\boldsymbol{\sigma}^+\dot{\boldsymbol{u}}_+\right) + \dot{\boldsymbol{u}}_+ \cdot \operatorname{div}\left(h(\varphi)\boldsymbol{\sigma}^+\right) \\
& - \operatorname{div}\left((1-h(\varphi))\boldsymbol{\sigma}^-\dot{\boldsymbol{u}}_-\right) + \dot{\boldsymbol{u}}_- \cdot \operatorname{div}\left((1-h(\varphi))\boldsymbol{\sigma}^-\right) \\
& - h(\varphi)\rho_+\left(\frac{\partial\psi^+}{\partial\boldsymbol{\varepsilon}^{*+}} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial\psi^+}{\partial\boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) \\
& - (1-h(\varphi))\rho_-\left(\frac{\partial\psi^-}{\partial\boldsymbol{\varepsilon}^{*-}} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial\psi^-}{\partial\boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) \mathrm{d}v \geq 0.
\end{aligned} \tag{42}$$

After application of the divergence theorem, Eq. (42) reads

$$\begin{aligned}
\int_{\delta\mathcal{S}} & \dot{\boldsymbol{u}}_+ \cdot \operatorname{div}\left(h(\varphi)\boldsymbol{\sigma}^+\right) + \dot{\boldsymbol{u}}_- \cdot \operatorname{div}\left((1-h(\varphi))\boldsymbol{\sigma}^-\right) \\
& - h(\varphi)\rho_+\left(\frac{\partial\psi^+}{\partial\boldsymbol{\varepsilon}^{*+}} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial\psi^+}{\partial\boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) \\
& - (1-h(\varphi))\rho_-\left(\frac{\partial\psi^-}{\partial\boldsymbol{\varepsilon}^{*-}} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial\psi^-}{\partial\boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) \mathrm{d}v \\
& - \int_{\partial\delta\mathcal{S}} h(\varphi)\left(\boldsymbol{\sigma}^+\boldsymbol{n}_{\mathcal{V}}\right) \cdot \dot{\boldsymbol{u}}_+ + (1-h(\varphi))\left(\boldsymbol{\sigma}^-\boldsymbol{n}_{\mathcal{V}}\right) \cdot \dot{\boldsymbol{u}}_- \,\mathrm{d}a \geq 0.
\end{aligned} \tag{43}$$

Regarding a material singular surface, the motion and, thus, the displacement field are continuous across the surface, implying that the velocity field is continuous as well, i.e. $\left[\boldsymbol{v}\right] = \boldsymbol{0}$ holds true, cf., e.g., the discussion in Truesdell and Toupin [37, p. 519]. Consequently, also

$$\left[\dot{\boldsymbol{u}}\right] = \boldsymbol{0}, \quad \dot{\boldsymbol{u}}_+ = \dot{\boldsymbol{u}}_- \tag{44}$$

holds true, cf. Bertram [62, eq. (3.1.12)]. Consequently, $\dot{\boldsymbol{u}} = \dot{\boldsymbol{u}}_+ = \dot{\boldsymbol{u}}_-$ is used, in the following. This kinematical condition is considered to hold true in the diffuse approximation of the sharp interface. Thus, taking into account Eq. (44) as well as the linearity of the divergence operator, and the definition of the stress vector, cf. Eq. (4), adopted for $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$, i.e., $\boldsymbol{t}^+ = \boldsymbol{\sigma}^+\boldsymbol{n}_{\mathcal{V}}^{\delta\mathcal{S}}$ and $\boldsymbol{t}^- = \boldsymbol{\sigma}^-\boldsymbol{n}_{\mathcal{V}}^{\delta\mathcal{S}}$, Eq. (43) can be written as

$$\begin{aligned}
\int_{\delta\mathcal{S}} & \dot{\boldsymbol{u}} \cdot \operatorname{div}(\overline{\boldsymbol{\sigma}}) - h(\varphi)\rho_+\left(\frac{\partial\psi^+}{\partial\boldsymbol{\varepsilon}^{*+}} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial\psi^+}{\partial\boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) \\
& - (1-h(\varphi))\rho_-\left(\frac{\partial\psi^-}{\partial\boldsymbol{\varepsilon}^{*-}} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial\psi^-}{\partial\boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) \mathrm{d}v - \int_{\partial\delta\mathcal{S}} \overline{\boldsymbol{t}} \cdot \dot{\boldsymbol{u}}\,\mathrm{d}a \geq 0.
\end{aligned} \tag{45}$$

with the interpolated stress $\overline{\boldsymbol{\sigma}}$ and the interpolated stress vector $\overline{\boldsymbol{t}}$ given by

$$\overline{\boldsymbol{\sigma}} := h(\varphi)\boldsymbol{\sigma}^+ + (1-h(\varphi))\boldsymbol{\sigma}^-, \quad \overline{\boldsymbol{t}} := h(\varphi)\boldsymbol{t}^+ + (1-h(\varphi))\boldsymbol{t}^-. \tag{46}$$

The inequality according to Eq. (45), and, thereby Eq. $(35)_3$, can be reduced by

$$\operatorname{div}(\overline{\boldsymbol{\sigma}}) = \boldsymbol{0},\ \forall \boldsymbol{x} \in \delta\mathcal{S}, \quad \overline{\boldsymbol{t}} = \boldsymbol{0},\ \forall \boldsymbol{x} \in \partial\delta\mathcal{S}_N, \quad \dot{\boldsymbol{u}} = \boldsymbol{0},\ \forall \boldsymbol{x} \in \partial\delta\mathcal{S}_D, \tag{47}$$

with $\partial\delta\mathcal{S}_N$ and $\partial\delta\mathcal{S}_D$ denoting the Neumann and the Dirichlet portion of the boundary, respectively. Thus, the reduced form of Eq. (45) is obtained as

$$\begin{aligned}
\int_{\delta\mathcal{S}} & - h(\varphi)\rho_+\left(\frac{\partial\psi^+}{\partial\boldsymbol{\varepsilon}^{*+}} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial\psi^+}{\partial\boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) \\
& - (1-h(\varphi))\rho_-\left(\frac{\partial\psi^-}{\partial\boldsymbol{\varepsilon}^{*-}} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial\psi^-}{\partial\boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) \mathrm{d}v \geq 0.
\end{aligned} \tag{48}$$

It should be noted that the specific free energy dependencies considered in Eq. (30) do not prescribe a particular constitutive material behavior, but provide the framework for possible constitutive laws. Moreover, since no decoupling between thermal and non-thermal contributions is assumed, the results obtained so far are valid for a thermomechanically coupled theory, as discussed by Prahs et al. [30]. In order to discuss the fulfillment of condition Eq. $(35)_3$, the contributions ψ^+ and ψ^- have to be specified in detail. In addition, the relation between the rates $\dot{\boldsymbol{\varepsilon}}^{*+}$, $\dot{\boldsymbol{\alpha}}^+$, $\dot{\boldsymbol{\varepsilon}}^{*-}$, and $\dot{\boldsymbol{\alpha}}^-$ have to be outlined. This will be addressed in the following sections regarding special cases.

2.2.11 Effect on the heat conduction equation

Application of the Legendre transformation, cf. Sect. 2.1, to the balance of internal energy, cf. Eq. (2) yields

$$\rho\dot{\psi} + \rho\dot{\theta}\eta + \rho\theta\dot{\eta} = \boldsymbol{\sigma} \cdot \dot{\boldsymbol{\varepsilon}} + \rho r - \operatorname{div}(\boldsymbol{q}) . \tag{49}$$

Regarding the diffuse interface, Eq. (A.18) is stated with respect to the interpolated quantities, illustrated by an overbar of the corresponding quantity, reading

$$\left(\overline{\rho\psi}\right)^{\bullet} + \dot{\theta}\,\overline{\rho\eta} + \theta\,(\overline{\rho\eta})^{\bullet} = \overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}} + \overline{\rho r} - \operatorname{div}(\overline{\boldsymbol{q}}) , \tag{50}$$

with the interpolation of the free energy density $\overline{f}_{\mathcal{V}} = \overline{\rho\psi}$ as given in Eq. (18) and the entropy density $\overline{\rho\eta}$ as

$$\overline{\rho\eta} = h(\varphi)\rho_+\eta^+ + (1 - h(\varphi))\rho_-\eta^- . \tag{51}$$

Thus, as commonly applied, the energy density is interpolated, but not the specific energy and density individually. As implied by Eq. (17), the interpolation of the entropy density $\overline{\rho\eta}$ is not an additional assumption. Instead, it is based on the potential relation of the entropy according to Eq. $(9)_2$ and the independence of the interpolation function and the phase-specific mass densities ρ_+ and ρ_- from the temperature. Since $\overline{\boldsymbol{\sigma}}$ is given as interpolation of the phase-specific stresses as stated in Eq. $(46)_1$, the interpolation of the strain is chosen accordingly as

$$\overline{\boldsymbol{\varepsilon}} = h(\varphi)\boldsymbol{\varepsilon}^+ + (1 - h(\varphi))\boldsymbol{\varepsilon}^- . \tag{52}$$

The interpolation of the heat source density is motivated by the interpolation of the free energy density, while the interpolation of the temperature flux is again motivated by the interpolation of the stress, both reading

$$\overline{\rho r} = h(\varphi)\rho_+ r^+ + (1 - h(\varphi))\rho_- r^- , \quad \overline{\boldsymbol{q}} = h(\varphi)\boldsymbol{q}^+ + (1 - h(\varphi))\boldsymbol{q}^- . \tag{53}$$

Taking into account Eqs. (51), (52), and (53), Eq. (50) can be reformulated as

$$\begin{aligned}
\overline{c}_\varepsilon\dot{\theta} = {} & \overline{\rho r} - \operatorname{div}(\overline{\boldsymbol{q}}) - l_0\frac{\partial h(\varphi)}{\partial\varphi}\dot{\varphi} \\
& - \left(h(\varphi)\rho_+\frac{\partial\psi^+}{\partial\varphi} + (1 - h(\varphi))\rho_-\frac{\partial\psi^-}{\partial\varphi} - h(\varphi)\theta\rho_+\frac{\partial^2\psi^+}{\partial\varphi\partial\theta} - (1 - h(\varphi))\theta\rho_-\frac{\partial^2\psi^-}{\partial\varphi\partial\theta} \right)\dot{\varphi} \\
& + h(\varphi)\frac{\partial\boldsymbol{\sigma}^+}{\partial\theta} \cdot \left(\dot{\boldsymbol{\varepsilon}}^+ - \dot{\boldsymbol{\varepsilon}}^{*+}\right)\theta + \rho_+ h(\varphi)\frac{\partial^2\psi^+}{\partial\boldsymbol{\alpha}^+\partial\theta} \cdot \dot{\boldsymbol{\alpha}}^+\theta \\
& + (1 - h(\varphi))\frac{\partial\boldsymbol{\sigma}^-}{\partial\theta} \cdot \left(\dot{\boldsymbol{\varepsilon}}^- - \cdot\dot{\boldsymbol{\varepsilon}}^{*-}\right)\theta + \rho_-(1 - h(\varphi))\frac{\partial^2\psi^-}{\partial\boldsymbol{\alpha}^-\partial\theta} \cdot \dot{\boldsymbol{\alpha}}^-\theta \\
& + h(\varphi)\left(\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^{*+} - \rho_+\frac{\partial\psi^+}{\partial\boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) + (1 - h(\varphi))\left(\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^{*-} - \rho_-\frac{\partial\psi^-}{\partial\boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) ,
\end{aligned} \tag{54}$$

with the interpolated specific heat

$$\overline{c}_\varepsilon = h(\varphi)\rho_+ c_\varepsilon^+ + (1 - h(\varphi))\rho_- c_\varepsilon^- \tag{55}$$

and the latent heat l_0 as

$$l_0 = \left[\rho e\right] - \left(\boldsymbol{\sigma}^+\boldsymbol{n}_{\mathcal{S}}\right) \cdot \left(\left[\boldsymbol{H}\right]\boldsymbol{n}_{\mathcal{S}}\right) \tag{56}$$

cf., e.g., Šilhavý [63, Eq. (22.1.11)] for small deformations. The detailed derivation of Eq. (54) is provided in the Appendix. Equation (54) is not limited to a specific mechanical or thermal behavior, since $\boldsymbol{\sigma}^+$, $\boldsymbol{\sigma}^-$, $\boldsymbol{q}^+$, and $\boldsymbol{q}^-$ are not yet specified up to this point.

3 Special cases regarding constitutive restrictions

3.1 Special case S_1: thermal decoupling of specific free energy

3.1.1 Constitutive assumptions

Subsequently, the following assumptions are considered:

A10 Only one scalar valued internal variable is considered each in $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$, referred to as p^+ and p^- instead of $\boldsymbol{\alpha}^+$ and $\boldsymbol{\alpha}^-$, respectively.

A11 The specific free energies ψ^+ and ψ^- can be additively decomposed accordingly

$$\psi^+ = \psi_{\mathrm{e}}^+ + \psi_{\mathrm{p}}^+ + \psi_\theta^+ + \psi_{\mathrm{ch}}^+, \quad \psi^- = \psi_{\mathrm{e}}^- + \psi_{\mathrm{p}}^- + \psi_\theta^- + \psi_{\mathrm{ch}}^-. \tag{57}$$

into elastic ψ_{e}^+, ψ_{e}^-, thermal ψ_θ^+, ψ_θ^-, and chemical contributions ψ_{ch}^+, ψ_{ch}^-, as well as contributions ψ_{p}^+, ψ_{p}^- that are associated with the internal variables p^+ and p^-, with the following dependencies

$$\psi^\pm = \psi_{\mathrm{e}}^\pm(\boldsymbol{\varepsilon}^\pm, \boldsymbol{\varepsilon}^{*\pm}, \varphi) \quad \psi_{\mathrm{p}}^\pm = \psi_{\mathrm{p}}^\pm(p^\pm, \varphi), \quad \psi_\theta^\pm = \psi_\theta^\pm(\theta, \varphi), \quad \psi_{\mathrm{ch}}^\pm = \text{const.} \tag{58}$$

Thus, the specific free energies ψ^+ and ψ^- are decomposed into a contribution that does not depend on the temperature, i.e., $\psi_{\mathrm{e}}^+ + \psi_{\mathrm{p}}^+ + \psi_{\mathrm{ch}}^+$ and $\psi_{\mathrm{e}}^- + \psi_{\mathrm{p}}^- + \psi_{\mathrm{ch}}^-$, and a contribution that depends only on the temperature and the order parameter, i.e., ψ_θ^+ and ψ_θ^-, respectively. In the context of regular points, where the order parameter is not present, a discussion of a similar decomposition is provided by [64]. Since the specific free energy density is decomposed into a thermal and non-thermal contributions, a thermomechanically weakly coupled theory is considered, subsequently, cf., e.g., [30]. The constant chemical contributions ψ_{ch}^+ and ψ_{ch}^- are considered, e.g., in the context of martensitic phase transformation, cf., e.g., Schneider et al. [65, Eq. (63)], Schoof et al. [29, Eq. (4)], Schoof et al. [66, Eq. (5)], providing a constant driving force.

A12 Regarding the elastic contribution of the specific free energy, the following relation between the derivatives with respect to $\boldsymbol{\varepsilon}^\pm$ and $\boldsymbol{\varepsilon}^{*\pm}$ is assumed

$$\rho \frac{\partial \psi_{\mathrm{e}}^\pm}{\partial \boldsymbol{\varepsilon}^\pm} = -\rho \frac{\partial \psi_{\mathrm{e}}^\pm}{\partial \boldsymbol{\varepsilon}^{*\pm}}. \tag{59}$$

A13 The inelastic strain tensors $\boldsymbol{\varepsilon}^{*+}$ and $\boldsymbol{\varepsilon}^{*-}$ depend on the internal variables p^+ and p^-, respectively, i.e.,

$$\boldsymbol{\varepsilon}^{*+} = \boldsymbol{\varepsilon}^{*+}(p^+), \quad \boldsymbol{\varepsilon}^{*-} = \boldsymbol{\varepsilon}^{*-}(p^-). \tag{60}$$

3.1.2 Points in $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$

The superscripts '+' and '−' associated with $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$ are omitted in this paragraph for better readability. As outlined in the Appendix, the Clausius–Duhem inequality according to Eq. (A.3) is exploited, accounting for A10–A13, reading

$$\rho\delta = \rho\delta_{\mathrm{m}} + \rho\delta_\theta \geq 0, \quad \rho\delta_{\mathrm{m}} := \boldsymbol{\sigma} \cdot \dot{\boldsymbol{\varepsilon}} - \rho\dot{\psi}_{\mathrm{e}} - \rho\dot{\psi}_{\mathrm{p}}, \quad \rho\delta_\theta := -\rho\dot{\psi}_\theta - \rho\dot{\theta}\eta - \frac{1}{\theta}\boldsymbol{q} \cdot \boldsymbol{g}. \tag{61}$$

Here, δ_{m} denotes the mechanical and δ_θ the thermal dissipation. As a consequence of the additive split according to A11, no coupling is present between δ_{m} and δ_θ, and

$$\rho\delta_{\mathrm{m}} = \boldsymbol{\sigma} \cdot \dot{\boldsymbol{\varepsilon}} - \rho\dot{\psi}_{\mathrm{e}} - \dot{\psi}_{\mathrm{p}} \geq 0, \quad \rho\delta_\theta = -\rho\dot{\psi}_\theta - \rho\dot{\theta}\eta - \frac{1}{\theta}\boldsymbol{q} \cdot \boldsymbol{g} \geq 0 \tag{62}$$

have to be fulfilled, independently. Application of the Coleman–Noll procedure to Eq. $(62)_1$ yields the potential relation for the Cauchy Stress tensor $\boldsymbol{\sigma}$ as well as the reduced mechanical dissipation inequality, reading

$$\boldsymbol{\sigma} = \rho \frac{\partial \psi_{\mathrm{e}}}{\partial \boldsymbol{\varepsilon}}, \quad \left(\boldsymbol{\sigma} \cdot \frac{\partial \boldsymbol{\varepsilon}^*}{\partial p} - \rho \frac{\partial \psi_{\mathrm{p}}}{\partial p} \right) \dot{p} \geq 0. \tag{63}$$

Regarding Eqs. $(63)_2$, (59) as well as Eq. $(63)_1$ are already considered. A possible choice for $\dot{p}$, that fulfills the reduced mechanical dissipation inequality Eq. $(63)_2$, is given, e.g., by

$$\dot{p} = \dot{p}_0 \left(\boldsymbol{\sigma} \cdot \frac{\partial \boldsymbol{\varepsilon}^*}{\partial p} - \rho \frac{\partial \psi_\mathrm{p}}{\partial p} \right), \quad \dot{p}_0 \geq 0 \tag{64}$$

with the non-negative referential rate $\dot{p}_0$. The application of the Coleman–Noll procedure to Eq. $(62)_2$ yields the potential relation for the entropy η as well as the reduced thermal dissipation inequality, reading

$$\eta = -\frac{\partial \psi_\theta}{\partial \theta}, \quad \rho \delta_\theta = -\frac{1}{\theta} \boldsymbol{q} \cdot \boldsymbol{g} \geq 0 \tag{65}$$

The non-negativity of Eq. $(65)_2$ is ensured by assuming Fourier's law, given by $\boldsymbol{q} = -\boldsymbol{K}\boldsymbol{g}$, where $\boldsymbol{K}$ denotes the positive semi-definite heat conduction tensor, cf., e.g., Bertram [62, p. 257].

3.1.3 Adaption of results to $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$

For the subsequent discussions regarding further special cases, the potential relations for the entropy and the Cauchy stress, according to Eq. $(65)_1$ and Eq. $(63)_1$, as well as the assumed Fourier's law are given explicitly for $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$, reading

$$\eta^\pm = -\frac{\partial \psi_\theta^\pm}{\partial \theta}, \quad \boldsymbol{q}^\pm = -\boldsymbol{K}^\pm \boldsymbol{g}, \quad \boldsymbol{\sigma}^\pm = \rho_\pm \frac{\partial \psi_\mathrm{e}^\pm}{\partial \boldsymbol{\varepsilon}^\pm}, \tag{66}$$

$$\dot{p}^\pm = \dot{p}_0^\pm \left(\boldsymbol{\sigma}^\pm \cdot \frac{\partial \boldsymbol{\varepsilon}^{*\pm}}{\partial p^\pm} - \rho_\pm \frac{\partial \psi_\mathrm{p}^\pm}{\partial p^\pm} \right), \quad \dot{p}_0^+, \dot{p}_0^- \geq 0, \tag{67}$$

with the non-negative referential rates $\dot{p}_0^+$, $\dot{p}_0^-$.

3.1.4 Points in $\delta\mathcal{S}$: evolution equation of the order parameter

As a consequence of A11, Eq. (36) is specified in terms of the contributions to the specific free energy. To illustrate the effect of the discussed special cases on the evolution equation of the order parameter, a parametrized evolution equation is introduced, reading

$$\dot{\varphi} = \dot{\varphi}_0 \left\{ \mathrm{div}\,(\boldsymbol{\Xi}) - \beta_\mathcal{S} \left(\frac{\partial \psi_\mathrm{grad}}{\partial \varphi} + \frac{\partial \psi_\mathrm{pot}}{\partial \varphi} \right) - \Delta_\psi - \Delta_\rho - \Delta_\mathrm{e} - \Delta_\mathrm{p} - \Delta_\theta \right\}, \tag{68}$$

with the referential rate $\dot{\varphi}_0 \geq 0$. The contributions $\beta_\mathcal{S}$, Δ_ψ, Δ_ρ, Δ_e, Δ_p, and Δ_θ are affected by the special case considered and given by Table 1. In this context, the special cases are briefly referred to as S_1, S_2, S_3, and S_4, with each special case representing a restriction of the previous one.

3.1.5 Points in $\delta\mathcal{S}$: fulfillment of $\mathcal{D}_{\delta\mathcal{S}}^\mathrm{mech} \geq 0$

Taking into account Eqs. (59), (60), and $(66)_3$, Eq. (48) reads

$$\begin{aligned} \int_{\delta\mathcal{S}} & - h(\varphi) \left(\rho_+ \frac{\partial \psi_\mathrm{p}^+}{\partial p^+} - \boldsymbol{\sigma}^+ \cdot \frac{\partial \boldsymbol{\varepsilon}^{*+}}{\partial p^+} \right) \dot{p}^+ \\ & - (1 - h(\varphi)) \left(\rho_- \frac{\partial \psi_\mathrm{p}^-}{\partial p^-} - \boldsymbol{\sigma}^- \cdot \frac{\partial \boldsymbol{\varepsilon}^{*-}}{\partial p^-} \right) \dot{p}^- \, \mathrm{d}v \geq 0. \end{aligned} \tag{69}$$

The inequality according to Eq. (69) can be satisfied by a suitable choice of the evolution equations for p^+ and p^-, which are already given by Eq. (67). Thus, the evolution equations for the internal variables p^+ and p^- within the diffuse interface $\delta\mathcal{S}$ are identical to the evolution equations for the internal variables within $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$.

Table 1 This table illustrates the contributions of the parametrized evolution equation, that are associated with the corresponding special case. Each special case constitutes a restriction of the former special case. In this context, S_1 represents the thermal decoupling of the specific free energy, S_2 identical mass densities, S_3 identical thermal contributions, and S_4 contributions ψ_{p}^{+} and ψ_{p}^{-} independent of the order parameter

	S_1	S_2	S_3	S_4
$\beta_{\mathcal{S}}$	$(h(\varphi)\rho_+ + (1-h(\varphi))\rho_-)\,\psi_{\mathcal{S}}$	$\rho\psi_{\mathcal{S}}$	cf. S_2	cf. S_2
Δ_ψ	$\left[\rho\psi\right]\frac{\partial h(\varphi)}{\partial\varphi}$	$\rho\left[\psi\right]\frac{\partial h(\varphi)}{\partial\varphi}$	cf. S_2	cf. S_2
Δ_ρ	$\left[\rho\right]\frac{\partial h(\varphi)}{\partial\varphi}\,\psi_{\mathcal{S}}\left(\psi_{\mathrm{grad}}+\psi_{\mathrm{pot}}\right)$	0	0	0
Δ_{e}	$h(\varphi)\rho_+\frac{\partial\psi_{\mathrm{e}}^{+}}{\partial\varphi}+(1-h(\varphi))\rho_-\frac{\partial\psi_{\mathrm{e}}^{-}}{\partial\varphi}$	$h(\varphi)\rho\frac{\partial\psi_{\mathrm{e}}^{+}}{\partial\varphi}+(1-h(\varphi))\rho\frac{\partial\psi_{\mathrm{e}}^{-}}{\partial\varphi}$	cf. S_2	cf. S_2
Δ_{p}	$h(\varphi)\rho_+\frac{\partial\psi_{\mathrm{p}}^{+}}{\partial\varphi}+(1-h(\varphi))\rho_-\frac{\partial\psi_{\mathrm{p}}^{-}}{\partial\varphi}$	$h(\varphi)\rho\frac{\partial\psi_{\mathrm{p}}^{+}}{\partial\varphi}+(1-h(\varphi))\rho\frac{\partial\psi_{\mathrm{p}}^{-}}{\partial\varphi}$	cf. S_2	0
Δ_θ	$h(\varphi)\rho_+\frac{\partial\psi_\theta^{+}}{\partial\varphi}+(1-h(\varphi))\rho_-\frac{\partial\psi_\theta^{-}}{\partial\varphi}$	$h(\varphi)\rho\frac{\partial\psi_\theta^{+}}{\partial\varphi}+(1-h(\varphi))\rho\frac{\partial\psi_\theta^{-}}{\partial\varphi}$	0	0

3.2 Special case S_2: identical mass densities

3.2.1 Constitutive assumption

The special case discussed in Sect. 3.1 is further restricted by the following assumption:

A14 The densities ρ_+ and ρ_- are the same and subsequently referred to as ρ, i.e.

$$\rho_+ = \rho_- =: \rho \tag{70}$$

Consequently, $\left[\rho\right] = 0$ holds true, implying both $h(\varphi)\rho_+ + (1-h(\varphi))\rho_- = \rho$ and $\left[\rho\psi\right] = \rho\psi^+ - \rho\psi^- = \rho\left[\psi\right]$.

The effect on the evolution equation of the order parameter is illustrated by Eq. (68) and Table 1.

3.3 Special case S_3: ψ_θ^+ and ψ_θ^- do not depend on the order parameter

3.3.1 Constitutive assumptions

The special case discussed in Sect. 3.2 is further restricted by the following assumption:

A15 The thermal contributions of the specific free energy ψ_θ^+ and ψ_θ^- are independent of the order parameter φ, i.e.

$$\psi_\theta^+ \neq \psi_\theta^+(\varphi), \quad \psi_\theta^- \neq \psi_\theta^-(\varphi) \tag{71}$$

and thereby $\partial\psi_\theta^+/\partial\varphi = \partial\psi_\theta^-/\partial\varphi = 0$ holds true.

The effect on the evolution equation of the order parameter is illustrated by Eq. (68) and Table 1.

3.4 Special case S_4: ψ_{p}^+ and ψ_{p}^- do not depend on the order parameter

3.4.1 Constitutive assumptions

The special case discussed in Sect. 3.3 is further restricted by the following assumption:

A16 The contributions ψ_{p}^{+} and ψ_{p}^{-} of the specific free energy are independent of the order parameter φ, i.e.

$$\psi_{\mathrm{p}}^{+} \neq \psi_{\mathrm{p}}^{+}(\varphi), \quad \psi_{\mathrm{p}}^{-} \neq \psi_{\mathrm{p}}^{-}(\varphi) \tag{72}$$

and thereby $\partial\psi_{\mathrm{p}}^{+}/\partial\varphi = \partial\psi_{\mathrm{p}}^{-}/\partial\varphi = 0$ holds true. This special case is considered in the context of the implementation of plastic material behavior in a phase-inherent manner, cf., e.g., Herrmann et al. [67, Eqs. (18) & (19)] regarding Mises plasticity and Prahs et al. [32] regarding classical crystal plasticity.

The effect on the evolution equation of the order parameter is illustrated by Eq. (68) and Table 1.

4 Comparison with classical variational approach

4.1 Classical derivation of the evolution equation

4.1.1 Consideration of domain containing diffuse interface

Subsequently, the free energy functional $\mathcal{F}$ with respect to the union

$$\mathcal{V} = \tilde{\mathcal{V}}^{+} \cup \tilde{\mathcal{V}}^{-} \cup \delta\mathcal{S} \tag{73}$$

is considered from the outset. The functional considers the free energy density f which accounts for the gradient and potential contributions ψ_{grad} and ψ_{pot} by means of $f_{\mathcal{S}}$, as well as the interpolation of the bulk contributions by means of $\overline{f}_{\mathcal{V}}$, reading

$$\mathcal{F} = \int_{\mathcal{V}} f \,\mathrm{d}v, \quad f = f_{\mathcal{S}} + \overline{f}_{\mathcal{V}}, \quad f_{\mathcal{S}} = \rho\psi_{\mathcal{S}}\left(\psi_{\mathrm{grad}} + \psi_{\mathrm{pot}}\right), \tag{74}$$

with $\overline{f}_{\mathcal{V}}$ according to Eq. (18). For the subsequent considerations, A7–A16 are taken into account. It is pointed out again that, due to A14, $\rho_{+} = \rho_{-} =: \rho$ is considered. The contribution $f_{\mathcal{S}}$ accounts for the transition from $\mathcal{S}$ to $\delta\mathcal{S}$. To compare the classical approach with the approach discussed in the previous sections, the form of $f_{\mathcal{S}}$ according to Eq. $(74)_3$ is chosen following Eq. (16), i.e., $\psi_{\mathcal{S}}$, ψ_{grad}, and ψ_{pot} are identical to those of Eq. (16). In the classical variational approach to PFM, the contribution $f_{\mathcal{S}}$ consists of the free energy densities f_{grad} and f_{pot}, reading

$$f_{\mathcal{S}} = f_{\mathrm{grad}} + f_{\mathrm{pot}}, \tag{75}$$

cf., e.g., Allen and Cahn [6, Eq. (4)], Penrose and Fife [10, Eq. (1.1)], Gurtin [11, Eq. (1.3)]. Consequently, the form of f_{grad} and ψ_{grad} as well as f_{pot} and ψ_{pot} differ, while $f_{\mathrm{grad}} = \rho\psi_{\mathcal{S}}\psi_{\mathrm{grad}}$ and $f_{\mathrm{pot}} = \rho\psi_{\mathcal{S}}\psi_{\mathrm{pot}}$ hold true, with the dimensionless contributions ψ_{grad} and ψ_{pot}. A detaild discussion regarding the implications of the choice of f_{grad} and f_{pot} on the triple junction benchmark is provided by [57].

4.1.2 Classical variational framework: equilibrium state

As mentioned in regard of Eq. (37), the classical derivation of the PFM considers an equilibrium state, at first, characterized by the vanishing variational derivative of a given (free-energy) functional,cf., e.g., Allen and Cahn [6, p. 1087], Penrose and Fife [10, Eq. (1.2)], reading

$$0 = \frac{\delta f}{\delta\varphi}, \quad \frac{\delta f}{\delta\varphi} = \left(\frac{\partial f}{\partial\varphi} - \operatorname{div}\left(\frac{\partial f}{\partial\nabla\varphi}\right)\right). \tag{76}$$

In this manuscript, $\delta f/\delta\varphi$ is referred to as variational derivative, cf. Goldstein et al. [68, Eqs. (13.63) & (13.64)]. Accounting additionally for Eqs. (20) and $(76)_2$ can be rewritten as

$$\begin{aligned}\frac{\delta f}{\delta\varphi} = {} & \rho\psi_{\mathcal{S}}\frac{\partial\psi_{\mathrm{grad}}}{\partial\varphi} - \operatorname{div}\left(\rho\psi_{\mathcal{S}}\frac{\partial\psi_{\mathrm{grad}}}{\partial\nabla\varphi}\right) + \rho\psi_{\mathcal{S}}\frac{\partial\psi_{\mathrm{pot}}}{\partial\varphi} + \rho\left[\psi\right]\frac{\partial h(\varphi)}{\partial\varphi} \\ & + \left(h(\varphi)\rho\frac{\partial\psi_{\mathrm{e}}^{+}}{\partial\varphi} + (1-h(\varphi))\rho\frac{\partial\psi_{\mathrm{e}}^{-}}{\partial\varphi}\right).\end{aligned} \tag{77}$$

4.1.3 Classical variational framework: nonequilibrium state

Regarding a nonequilibrium state, the classical PFM approach postulates an evolution equation that relates the variational derivative proportional to the rate of the order parameter by means of a constant of proportionality, reading

$$\dot{\varphi} = \dot{\varphi}_0 \frac{\delta f}{\delta \varphi}. \tag{78}$$

Here, $\dot{\varphi}_0$ is referred to as referential rate, as previously introduced in regard of Eq. (36). Inserting Eq. (77) in Eq. (78) yields

$$\begin{aligned}\dot{\varphi} = \dot{\varphi}_0 \Bigg\{ &\operatorname{div}\left(\rho\psi_{\mathcal{S}} \frac{\partial \psi_{\text{grad}}}{\partial \nabla\varphi}\right) - \rho\psi_{\mathcal{S}}\left(\frac{\partial \psi_{\text{grad}}}{\partial \varphi} + \frac{\partial \psi_{\text{pot}}}{\partial \varphi}\right) - \rho\big[\psi\big]\frac{\partial h(\varphi)}{\partial \varphi} \\ &- \left(h(\varphi)\rho\frac{\partial \psi_{\text{e}}^{+}}{\partial \varphi} + (1-h(\varphi))\rho\frac{\partial \psi_{\text{e}}^{-}}{\partial \varphi}\right)\Bigg\}, \quad \dot{\varphi}_0 \geq 0. \end{aligned} \tag{79}$$

4.2 Comparison of obtained evolution equation

4.2.1 Comparison of driving force contributions

Since Assumptions A7–A16 are considered, $\boldsymbol{\Xi} = \rho\psi_{\mathcal{S}}\partial\psi_{\text{grad}}/\partial\nabla\varphi$ and $\beta_{\mathcal{S}} = \rho\psi_{\mathcal{S}}$ hold true. Moreover, the thrid and fourth contribution in Eq. (79) correspond to Δ_{ψ} and Δ_{e}, cf. Table 1. Consequently, the evolution equations stated in Eqs. (79) and (68) are identical.

4.2.2 Comparison with classical Allen–Cahn/Ginzburg–Landau equation

Following A1, the mass density is considered to be constant. Using the abbreviation $\boldsymbol{\xi} = \partial\psi_{\text{grad}}/\partial\nabla\varphi$, cf. Sect. 2.2, the application of the product rule with respect to the divergence term of Eq. (79) yields

$$\operatorname{div}\left(\rho\psi_{\mathcal{S}}\boldsymbol{\xi}\right) = \rho\frac{\partial\psi_{\mathcal{S}}}{\partial\theta}\boldsymbol{g}\cdot\boldsymbol{\xi} + \rho\psi_{\mathcal{S}}\operatorname{div}\left(\boldsymbol{\xi}\right), \tag{80}$$

with $\boldsymbol{g} = \operatorname{grad}(\theta)$. Consequently, inserting Eq. (80) in Eq. (79) yields

$$\begin{aligned}\dot{\varphi} = \dot{\varphi}_0 \Bigg\{ &\rho\frac{\partial\psi_{\mathcal{S}}}{\partial\theta}\boldsymbol{g}\cdot\boldsymbol{\xi} + \rho\psi_{\mathcal{S}}\operatorname{div}\left(\boldsymbol{\xi}\right) - \rho\psi_{\mathcal{S}}\frac{\partial\psi_{\text{grad}}}{\partial\varphi} - \rho\psi_{\mathcal{S}}\frac{\partial\psi_{\text{pot}}}{\partial\varphi} - \rho\big[\psi\big]\frac{\partial h(\varphi)}{\partial\varphi} \\ &- \left(h(\varphi)\rho\frac{\partial\psi_{\text{e}}^{+}}{\partial\varphi} + (1-h(\varphi))\rho\frac{\partial\psi_{\text{e}}^{-}}{\partial\varphi}\right)\Bigg\}. \end{aligned} \tag{81}$$

The classical Allen–Cahn equation does not account for the contribution $(\rho\partial\psi_{\mathcal{S}}/\partial\theta)\ \boldsymbol{g}\cdot\boldsymbol{\xi}$, cf. Allen and Cahn [6, Eq. (12)]. To obtain the identical evolution equation, subsequently, the following assumption is considered:

A17 The temperature is constant in space

$$\theta \neq \theta(\boldsymbol{x}) \tag{82}$$

and thereby $\boldsymbol{g} = \boldsymbol{0}$ holds true.

Taking into account A17, the evolution according to Eq. (81) reads

$$\begin{aligned}\dot{\varphi} = \dot{\varphi}_0 \Bigg\{ &\rho\psi_{\mathcal{S}}\operatorname{div}\left(\boldsymbol{\xi}\right) - \rho\psi_{\mathcal{S}}\frac{\partial\psi_{\text{grad}}}{\partial\varphi} - \rho\psi_{\mathcal{S}}\frac{\partial\psi_{\text{pot}}}{\partial\varphi} - \rho\big[\psi\big]\frac{\partial h(\varphi)}{\partial\varphi} \\ &- \left(h(\varphi)\rho\frac{\partial\psi_{\text{e}}^{+}}{\partial\varphi} + (1-h(\varphi))\rho\frac{\partial\psi_{\text{e}}^{-}}{\partial\varphi}\right)\Bigg\}, \end{aligned} \tag{83}$$

which corresponds to the Allen–Cahn respectively Ginzburg–Landau equation, cf., e.g., Allen and Cahn [6, Eq.(12)], Penrose and Fife [10, Eq.(1.5)], Gurtin [11, Eq.(1.7)].

5 Concluding remarks

5.1 Phase-field method as approximation of the sharp interface theory

Following Maugin [42, p. 80], the order parameter is introduced as ISV but not as DOF, here. Therefore, the derivation of the phase-field method is based on a Cauchy continuum instead of an extended continuum. The phase transformation front, which can be generally modeled by a non-material singular surface in the sharp interface context, is considered to evolve slowly, quasi-static and has no body forces acting on it. In this regard, the associated balances of mass, linear momentum and internal energy are formally similar to those of a material singular surface. For this special case, the current work discusses the PFM as an approximation of the sharp interface theory. The evolution equation of the order parameter, describing the evolving diffuse interface, is obtained by exploitation of the Clausius–Duhem inequality. Thus, a generalization of the commonly considered evolution equation of the order parameter can be obtained in a consistent manner in view of continuum thermodynamics. The impact of the presented approach on the heat conduction equation in the diffuse interface region is analyzed. This involves a latent heat contribution that is intrinsically introduced due to the evolution of the order parameters. For simplicity, a two-phase material is considered.

5.2 Comparison with classical approach

The evolution equation obtained by the presented approach and the classical approach is compared for the assumptions: (1) thermal decoupling of the specific free energy, (2) identical mass densities, (3) ψ_θ^+ and ψ_θ^- independent of the order parameter, and (4) ψ_p^+ and ψ_p^- independent of the order parameter. It is shown that

- The evolution equation of the order parameter given by Eq. (79), obtained by the classical approach, coincides with the evolution equation obtained by the presented approach, given by Eq. (68).
- The obtained evolution equation stated by Eq. (79) contains an additional, temperature-dependent contribution, compared to the classical Allen–Cahn equation. Assuming additionally a homogeneous temperature distribution with respect to space, inducing a vanishing temperature gradient $\boldsymbol{g}$, the obtained evolution equation coincides with the classical Allen–Cahn/Ginzburg–Landau equation.

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Author contributions Andreas Prahs: Conceptualization, formal analysis, investigation, methodology, validation, writing—original draft. Daniel Schneider: Conceptualization, writing—review and editing, funding acquisition. Britta Nestler: Writing—review and editing, funding acquisition.

Data Availibility Statement

No datasets were generated or analysed during the current study.

Declarations

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

Appendix

Clausius–Duhem inequality

Notation

The discussions in this and the following section, which cover Eqs. (A.1)–(A.17), are applicable to points in both $\mathcal{V}^+$ and $\mathcal{V}^-$, as well as points in $\tilde{\mathcal{V}}^+$ and $\tilde{\mathcal{V}}^-$. To enhance readability, the superscripts '+' and '−' are omitted in these sections.

Clausius–Duhem inequality in regular points

Regarding regular points, the local form of the entropy balance is given by

$$\rho\delta = \rho\theta\dot{\eta} - \rho r + \theta \mathrm{div}\left(\frac{\boldsymbol{q}}{\theta}\right), \tag{A.1}$$

with $\delta := p^{\eta}_{\mathcal{V}}\theta$ denoting the bulk dissipation. Subsequently, the Legendre transformation is taken into acount, cf., e.g., Beegle et al. [55], establishing the relation between the specific free energy ψ, the specific internal energy e and the specific entropy η via $\psi = e - \theta\eta$. According to the Second Law of Thermodynamics, the dissipation must always be non-negative. This leads to the dissipation inequality in regular points, cf., e.g., Prahs and Böhlke [52, Eq. (10)], reading

$$\rho\delta = \rho\dot{e} - \rho\dot{\psi} - \rho\dot{\theta}\eta - \rho r + \mathrm{div}\,(\boldsymbol{q}) - \frac{1}{\theta}\boldsymbol{q}\cdot\boldsymbol{g} \geq 0, \tag{A.2}$$

where $\boldsymbol{g} = \mathrm{grad}\,(\theta)$ is introduced, cf., e.g., Coleman and Gurtin [69, eq. (2.5)]. This form of the dissipation is often denoted as Clausius–Duhem inequality (CDI) [69]. Inserting the balance of internal energy, cf. Eq. (2)[3]. in the previous equation yields

$$\rho\delta = \boldsymbol{\sigma}\cdot\dot{\boldsymbol{\varepsilon}} - \rho\dot{\psi} - \rho\dot{\theta}\eta - \frac{1}{\theta}\boldsymbol{q}\cdot\boldsymbol{g} \geq 0. \tag{A.3}$$

Clausius–Duhem inequality in singular points

Regarding the singular surface, the dissipation is defined as $\delta_{\mathcal{S}} := p^{\eta}_{\mathcal{S}}\theta$. The following assumption is considered, subsequently:

A17 The temperature is continuous across the material singular surface, i.e., $\left[\theta\right] = 0$, cf. Müller [43, p. 11] and Struchtrup [70, p. 494].

Thus, the local form of the entropy balance is given by

$$\rho_{\mathcal{S}}\delta_{\mathcal{S}} = \rho_{\mathcal{S}}\theta\dot{\eta}_{\mathcal{S}} - \rho_{\mathcal{S}}r_{\mathcal{S}} + \left[\boldsymbol{q}\right]\cdot\boldsymbol{n}_{\mathcal{S}} \tag{A.4}$$

Similar to the Legendre transformation for regular points, the relation between $e_{\mathcal{S}}$, $\psi_{\mathcal{S}}$, and $\eta_{\mathcal{S}}$ is given by $\psi_{\mathcal{S}} = e_{\mathcal{S}} - \theta\eta_{\mathcal{S}}$. Regarding singular points, the dissipation has to be non-negative as well. Thus, the dissipation inequality is obtained in singular points as

$$\rho_{\mathcal{S}}\delta_{\mathcal{S}} = \rho_{\mathcal{S}}\dot{e}_{\mathcal{S}} - \rho_{\mathcal{S}}\dot{\psi}_{\mathcal{S}} - \rho_{\mathcal{S}}\dot{\theta}\eta_{\mathcal{S}} - \rho_{\mathcal{S}}r_{\mathcal{S}} + \left[\boldsymbol{q}\right]\cdot\boldsymbol{n}_{\mathcal{S}} \geq 0. \tag{A.5}$$

Moreover, taking into account balance of internal energy on a material singular surface, cf. Eq. (3)[4], the previous equation reads

$$\rho_{\mathcal{S}}\delta_{\mathcal{S}} = -\rho_{\mathcal{S}}\dot{\psi}_{\mathcal{S}} - \rho_{\mathcal{S}}\dot{\theta}\eta_{\mathcal{S}} \geq 0. \tag{A.6}$$

[3] Referring to the manuscript and not the Appendix.
[4] Referring to the manuscript and not the Appendix.

Exploitation of the Clausius–Duhem inequality

Regular points

Subsequently, the following assumptions are considered:

A18 In the context of small deformations, the additive decomposition of the infinitesmal strain tensor in an elastic contribution $\boldsymbol{\varepsilon}^{\mathrm{e}}$ and an inelastic contribution $\boldsymbol{\varepsilon}^{*}$ is considered, reading

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^{\mathrm{e}} + \boldsymbol{\varepsilon}^{*}. \tag{A.7}$$

A19 The specific free energy ψ depends on the the total strain $\boldsymbol{\varepsilon}$, the inelastic strain $\boldsymbol{\varepsilon}^{*}$, the temperature θ, and the vector of internal state variables $\boldsymbol{\alpha}$. Thus,

$$\psi = \psi(\boldsymbol{\varepsilon}, \boldsymbol{\varepsilon}^{*}, \theta, \boldsymbol{\alpha}) \tag{A.8}$$

holds true.

Taking into account Eqs. (A.7) and (A.8), Eq. (A.3) reads

$$\left(\boldsymbol{\sigma} - \rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}}\right) \cdot \dot{\boldsymbol{\varepsilon}} - \rho \left(\eta + \frac{\partial \psi}{\partial \theta}\right) \dot{\theta} - \rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}^{*}} \cdot \dot{\boldsymbol{\varepsilon}}^{*} - \rho \frac{\partial \psi}{\partial \boldsymbol{\alpha}} \cdot \dot{\boldsymbol{\alpha}} - \frac{1}{\theta} \boldsymbol{q} \cdot \boldsymbol{g} \geq 0. \tag{A.9}$$

The validity of the CDI for arbitrary rates of the considered fields as well of their gradients is implied by the application of the Coleman–Noll procedure, cf., e.g., Coleman and Gurtin [69, Eqs. (5.11)–(5.14)]. The fulfillment of the CDI according to Eq. (A.9) for arbitrary rates $\dot{\boldsymbol{\varepsilon}}$ and $\dot{\theta}$ leads to the potential relations for the Cauchy stress $\boldsymbol{\sigma}$ and the entropy η, reading.

$$\boldsymbol{\sigma} = \rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}}, \quad \eta = -\frac{\partial \psi}{\partial \theta} \tag{A.10}$$

In the following, the subsequent assumption is considered:

A20 The inelastic contribution $\boldsymbol{\varepsilon}^{*}$ depends on $\boldsymbol{\alpha}$, i.e.

$$\boldsymbol{\varepsilon}^{*} = \boldsymbol{\varepsilon}^{*}(\boldsymbol{\alpha}) \tag{A.11}$$

holds true.

Taking Eqs. (A.10) and (A.11) into account, Eq. (A.9) yields the reduced dissipation inequality, reading

$$\left(-\rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}^{*}} \cdot \frac{\partial \boldsymbol{\varepsilon}^{*}}{\partial \boldsymbol{\alpha}} - \rho \frac{\partial \psi}{\partial \boldsymbol{\alpha}}\right) \cdot \dot{\boldsymbol{\alpha}} - \frac{1}{\theta} \boldsymbol{q} \cdot \boldsymbol{g} \geq 0. \tag{A.12}$$

Further exploitation of Eq. (A.12) is considered in a subsequent section regarding specific choices of material behavior. Subsequently, the following assumption is considered:

A21 Regarding the specific free energy, the following relation between the derivatives with respect to $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}^{*}$ is assumed

$$\rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} = -\rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}^{*}}. \tag{A.13}$$

Accounting for A21 and Eqs. (A.10) and (A.12) can be written as

$$\left(\boldsymbol{\sigma} \cdot \frac{\partial \boldsymbol{\varepsilon}^{*}}{\partial \boldsymbol{\alpha}} - \rho \frac{\partial \psi}{\partial \boldsymbol{\alpha}}\right) \cdot \dot{\boldsymbol{\alpha}} - \frac{1}{\theta} \boldsymbol{q} \cdot \boldsymbol{g} \geq 0. \tag{A.14}$$

A further exploitation of the reduced dissipation inequality given by Eq. (A.14) requires a specification of the specific free energy and is, thus, considered in a subsequent section.

Singular points

The application of the Coleman–Noll procedure to Eq. (A.6) yields that $\psi_{\mathcal{S}}$ can only depend on the temperature, i.e.,

$$\psi_{\mathcal{S}} = \psi_{\mathcal{S}}(\theta), \tag{A.15}$$

holds true. Thus, Eq. (A.6) yields the potential relation for $\eta_{\mathcal{S}}$, reading

$$\eta_{\mathcal{S}} = -\frac{\partial \psi_{\mathcal{S}}}{\partial \theta}. \tag{A.16}$$

Moreover, Eq. (A.16) implicitly states that

$$\dot{\psi}_{\mathcal{S}} = \frac{\partial \psi_{\mathcal{S}}}{\partial \theta}\dot{\theta} = -\eta_{\mathcal{S}}\dot{\theta}. \tag{A.17}$$

holds true and, consequently, the dissipation $\delta_{\mathcal{S}}$ according to Eq. (A.6) is vanishing. Thus, the considered material singular surface meets the criteria of an ideal wall according to Müller [43], cf. also the comment by Prahs and Böhlke [50, p. 1432].

Heat conduction and latent heat

Derivation of the equation of heat conduction

Application of the chain rule to Eq. (50) yields

$$\begin{aligned}
&\rho_+ \frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi}\psi^+ + \left(\frac{\partial \psi^+}{\partial \boldsymbol{\varepsilon}^+}\cdot\dot{\boldsymbol{\varepsilon}}^+ + \frac{\partial \psi^+}{\partial \boldsymbol{\varepsilon}^{*+}}\cdot\dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial \psi^+}{\partial \varphi}\dot{\varphi} + \frac{\partial \psi^+}{\partial \boldsymbol{\alpha}^+}\cdot\dot{\boldsymbol{\alpha}}^+ + \frac{\partial \psi^+}{\partial \theta}\dot{\theta}\right) h(\varphi)\rho_+ \\
&\quad - \rho_- \frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi}\psi^- + \left(\frac{\partial \psi^-}{\partial \boldsymbol{\varepsilon}^-}\cdot\dot{\boldsymbol{\varepsilon}}^- + \frac{\partial \psi^-}{\partial \boldsymbol{\varepsilon}^{*-}}\cdot\dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial \psi^-}{\partial \varphi}\dot{\varphi} + \frac{\partial \psi^-}{\partial \boldsymbol{\alpha}^-}\cdot\dot{\boldsymbol{\alpha}}^- + \frac{\partial \psi^-}{\partial \theta}\dot{\theta}\right)(1-h(\varphi))\rho_- \\
&\quad + h(\varphi)\rho_+\eta^+\dot{\theta} + (1-h(\varphi))\rho_-\eta^-\dot{\theta} \\
&\quad + \left(\rho_+ \frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi}\eta^+ - \rho_- \frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi}\eta^- + \rho_+ h(\varphi)\dot{\eta}^+ + \rho_-(1-h(\varphi))\dot{\eta}^-\right)\theta \\
&= \overline{\boldsymbol{\sigma}}\cdot\dot{\overline{\boldsymbol{\varepsilon}}} + \overline{\rho r} - \operatorname{div}(\overline{\boldsymbol{q}})
\end{aligned} \tag{A.18}$$

Accounting for Eq. $(9)_1$, i.e., $\rho_+ \partial\psi^+/\partial\boldsymbol{\varepsilon}^+ = \boldsymbol{\sigma}^+$, and $\rho_- \partial\psi^-/\partial\boldsymbol{\varepsilon}^- = \boldsymbol{\sigma}^-$, as well as for Eq. $(9)_2$, i.e., $\partial\psi^+/\partial\theta = -\eta^+$ and $\partial\psi^-/\partial\theta = -\eta^-$, yields

$$\begin{aligned}
&\left[\rho\psi\right]\frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi} + \left[\rho\eta\right]\frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi}\theta + h(\varphi)\boldsymbol{\sigma}^+\cdot\dot{\boldsymbol{\varepsilon}}^+ + (1-h(\varphi))\boldsymbol{\sigma}^-\cdot\dot{\boldsymbol{\varepsilon}}^- \\
&\quad + \left(\frac{\partial \psi^+}{\partial \boldsymbol{\varepsilon}^{*+}}\cdot\dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial \psi^+}{\partial \varphi}\dot{\varphi} + \frac{\partial \psi^+}{\partial \boldsymbol{\alpha}^+}\cdot\dot{\boldsymbol{\alpha}}^+\right) h(\varphi)\rho_+ \\
&\quad + \left(\frac{\partial \psi^-}{\partial \boldsymbol{\varepsilon}^{*-}}\cdot\dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial \psi^-}{\partial \varphi}\dot{\varphi} + \frac{\partial \psi^-}{\partial \boldsymbol{\alpha}^-}\cdot\dot{\boldsymbol{\alpha}}^-\right)(1-h(\varphi))\rho_- \\
&\quad + \rho_+\theta h(\varphi)\dot{\eta}^+ + \rho_-\theta(1-h(\varphi))\dot{\eta}^- \\
&= \overline{\boldsymbol{\sigma}}\cdot\dot{\overline{\boldsymbol{\varepsilon}}} + \overline{\rho r} - \operatorname{div}(\overline{\boldsymbol{q}})
\end{aligned} \tag{A.19}$$

Moreover, with $\dot{\eta}^+ = \left(-\frac{\partial \psi^+}{\partial \theta}\right)^{\cdot} = -\frac{\partial \dot{\psi}^+}{\partial \theta}$ and $\dot{\eta}^- = \left(-\frac{\partial \psi^-}{\partial \theta}\right)^{\cdot} = -\frac{\partial \dot{\psi}^-}{\partial \theta}$, Eq. (A.19) reads

$$
\begin{aligned}
&\left[\rho\psi\right]\frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi} + \left[\rho\eta\right]\frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi}\theta + h(\varphi)\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ + (1-h(\varphi))\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- \\
&\quad + h(\varphi)\rho_+\left(\frac{\partial \psi^+}{\partial \boldsymbol{\varepsilon}^{*+}} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial \psi^+}{\partial \varphi}\dot{\varphi} + \frac{\partial \psi^+}{\partial \boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) \\
&\quad + (1-h(\varphi))\rho_-\left(\frac{\partial \psi^-}{\partial \boldsymbol{\varepsilon}^{*-}} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial \psi^-}{\partial \varphi}\dot{\varphi} + \frac{\partial \psi^-}{\partial \boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) \\
&\quad - \rho_+\theta\left(\frac{\partial^2 \psi^+}{\partial \boldsymbol{\varepsilon}^+ \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^+ + \frac{\partial^2 \psi^+}{\partial \boldsymbol{\varepsilon}^{*+} \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \frac{\partial^2 \psi^+}{\partial \varphi \partial \theta}\dot{\varphi} + \frac{\partial^2 \psi^+}{\partial \boldsymbol{\alpha}^+ \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^+ + \frac{\partial^2 \psi^+}{\partial \theta^2}\dot{\theta}\right) h(\varphi) \\
&\quad - \rho_-\theta\left(\frac{\partial^2 \psi^-}{\partial \boldsymbol{\varepsilon}^- \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^- + \frac{\partial^2 \psi^-}{\partial \boldsymbol{\varepsilon}^{*-} \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \frac{\partial^2 \psi^-}{\partial \varphi \partial \theta}\dot{\varphi} + \frac{\partial^2 \psi^-}{\partial \boldsymbol{\alpha}^- \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^- + \frac{\partial^2 \psi^-}{\partial \theta^2}\dot{\theta}\right)(1-h(\varphi)) \\
&\quad = \overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}} + \overline{\rho r} - \operatorname{div}(\overline{\boldsymbol{q}})
\end{aligned}
\tag{A.20}
$$

Accounting for the definition of the specific heats $c_\varepsilon^+ = -\theta\partial^2\psi^+/\partial\theta^2$, $c_\varepsilon^- = -\theta\partial^2\psi^-/\partial\theta^2$, and introducing the interpolated specific heat $\overline{c}_\varepsilon = h(\varphi)\rho_+ c_\varepsilon^+ + (1-h(\varphi))\rho_- c_\varepsilon^-$, rearrangement of Eq. (A.20) yields

$$
\begin{aligned}
&\overline{c}_\varepsilon\dot{\theta} + \left[\rho\psi\right]\frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi} + \left[\rho\eta\right]\frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi}\theta \\
&\quad = \overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}} + \overline{\rho r} - \operatorname{div}(\overline{\boldsymbol{q}}) - h(\varphi)\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ - (1-h(\varphi))\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- \\
&\quad + h(\varphi)\left(\rho_+\frac{\partial^2 \psi^+}{\partial \boldsymbol{\varepsilon}^+ \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^+ + \rho_+\frac{\partial^2 \psi^+}{\partial \boldsymbol{\varepsilon}^{*+} \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^{*+}\right)\theta + \rho_+ h(\varphi)\frac{\partial^2 \psi^+}{\partial \boldsymbol{\alpha}^+ \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^+\theta \\
&\quad + (1-h(\varphi))\left(\rho_-\frac{\partial^2 \psi^-}{\partial \boldsymbol{\varepsilon}^- \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^- + \rho_-\frac{\partial^2 \psi^-}{\partial \boldsymbol{\varepsilon}^{*-} \partial \theta} \cdot \dot{\boldsymbol{\varepsilon}}^{*-}\right)\theta + \rho_-(1-h(\varphi))\frac{\partial^2 \psi^-}{\partial \boldsymbol{\alpha}^- \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^-\theta \\
&\quad - h(\varphi)\left(\rho_+\frac{\partial \psi^+}{\partial \boldsymbol{\varepsilon}^{*+}} \cdot \dot{\boldsymbol{\varepsilon}}^{*+} + \rho_+\frac{\partial \psi^+}{\partial \boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) - (1-h(\varphi))\left(\rho_-\frac{\partial \psi^-}{\partial \boldsymbol{\varepsilon}^{*-}} \cdot \dot{\boldsymbol{\varepsilon}}^{*-} + \rho_-\frac{\partial \psi^-}{\partial \boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) \\
&\quad - \left(h(\varphi)\rho_+\frac{\partial \psi^+}{\partial \varphi} + (1-h(\varphi))\rho_-\frac{\partial \psi^-}{\partial \varphi} - h(\varphi)\theta\rho_+\frac{\partial^2 \psi^+}{\partial \varphi \partial \theta} - (1-h(\varphi))\theta\rho_-\frac{\partial^2 \psi^-}{\partial \varphi \partial \theta}\right)\dot{\varphi}
\end{aligned}
\tag{A.21}
$$

Using the Legendre transformation, i.e., $e^\pm = \psi^\pm + \theta\eta^\pm$, $\left[\rho\psi\right] + \left[\rho\eta\right]\theta = \left[\rho e\right]$ holds true. Moreover, taking into account Eqs. $(9)_1$ and (A.13), i.e., $\rho_+\partial\psi^+/\partial\boldsymbol{\varepsilon}^{*+} = -\boldsymbol{\sigma}^+$ and $\rho_-\partial\psi^-/\partial\boldsymbol{\varepsilon}^{*-} = -\boldsymbol{\sigma}^-$, Eq. (A.21) can be rewritten as

$$
\begin{aligned}
&\overline{c}_\varepsilon\dot{\theta} = \overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}} + \overline{\rho r} - \operatorname{div}(\overline{\boldsymbol{q}}) - h(\varphi)\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ - (1-h(\varphi))\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- - \left[\rho e\right]\frac{\partial h(\varphi)}{\partial \varphi}\dot{\varphi} \\
&\quad + h(\varphi)\frac{\partial \boldsymbol{\sigma}^+}{\partial \theta} \cdot \left(\dot{\boldsymbol{\varepsilon}}^+ - \dot{\boldsymbol{\varepsilon}}^{*+}\right)\theta + \rho_+ h(\varphi)\frac{\partial^2 \psi^+}{\partial \boldsymbol{\alpha}^+ \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^+\theta \\
&\quad + (1-h(\varphi))\frac{\partial \boldsymbol{\sigma}^-}{\partial \theta} \cdot \left(\dot{\boldsymbol{\varepsilon}}^- - \dot{\boldsymbol{\varepsilon}}^{*-}\right)\theta + \rho_-(1-h(\varphi))\frac{\partial^2 \psi^-}{\partial \boldsymbol{\alpha}^- \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^-\theta \\
&\quad + h(\varphi)\left(\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^{*+} - \rho_+\frac{\partial \psi^+}{\partial \boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+\right) + (1-h(\varphi))\left(\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^{*-} - \rho_-\frac{\partial \psi^-}{\partial \boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^-\right) \\
&\quad - \left(h(\varphi)\rho_+\frac{\partial \psi^+}{\partial \varphi} + (1-h(\varphi))\rho_-\frac{\partial \psi^-}{\partial \varphi} - h(\varphi)\theta\rho_+\frac{\partial^2 \psi^+}{\partial \varphi \partial \theta} - (1-h(\varphi))\theta\rho_-\frac{\partial^2 \psi^-}{\partial \varphi \partial \theta}\right)\dot{\varphi}.
\end{aligned}
\tag{A.22}
$$

Reformulating the stress power $\overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}}$ by means of Eq. (52) and introducing the latent heat as $l_0 = \left[\!\left[\rho e\right]\!\right] - \left(\boldsymbol{\sigma}^+ \boldsymbol{n}_{\mathcal{S}}\right) \cdot \left(\left[\!\left[\boldsymbol{H}\right]\!\right] \boldsymbol{n}_{\mathcal{S}}\right)$, cf., e.g., Šilhavý [63, Eq. (22.1.11)], Eq. (A.22) reads

$$
\begin{aligned}
\overline{c}_\varepsilon \dot{\theta} = {} & \overline{\rho r} - \operatorname{div}\left(\overline{\boldsymbol{q}}\right) - l_0 \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi} \\
& - \left(h(\varphi) \rho_+ \frac{\partial \psi^+}{\partial \varphi} + (1 - h(\varphi)) \rho_- \frac{\partial \psi^-}{\partial \varphi} - h(\varphi) \theta \rho_+ \frac{\partial^2 \psi^+}{\partial \varphi \partial \theta} - (1 - h(\varphi)) \theta \rho_- \frac{\partial^2 \psi^-}{\partial \varphi \partial \theta} \right) \dot{\varphi} \\
& + h(\varphi) \frac{\partial \boldsymbol{\sigma}^+}{\partial \theta} \cdot \left(\dot{\boldsymbol{\varepsilon}}^+ - \dot{\boldsymbol{\varepsilon}}^{*+} \right) \theta + \rho_+ h(\varphi) \frac{\partial^2 \psi^+}{\partial \boldsymbol{\alpha}^+ \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^+ \theta \\
& + (1 - h(\varphi)) \frac{\partial \boldsymbol{\sigma}^-}{\partial \theta} \cdot \left(\dot{\boldsymbol{\varepsilon}}^- - \dot{\boldsymbol{\varepsilon}}^{*-} \right) \theta + \rho_- (1 - h(\varphi)) \frac{\partial^2 \psi^-}{\partial \boldsymbol{\alpha}^- \partial \theta} \cdot \dot{\boldsymbol{\alpha}}^- \theta \\
& + h(\varphi) \left(\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^{*+} - \rho_+ \frac{\partial \psi^+}{\partial \boldsymbol{\alpha}^+} \cdot \dot{\boldsymbol{\alpha}}^+ \right) + (1 - h(\varphi)) \left(\boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^{*-} - \rho_- \frac{\partial \psi^-}{\partial \boldsymbol{\alpha}^-} \cdot \dot{\boldsymbol{\alpha}}^- \right) .
\end{aligned} \tag{A.23}
$$

The required calculations, which are essential for the conversion of Eqs. (A.22) to (A.23), are provided in the following paragraph.

Considered auxiliary calculations

To derive Eq. (A.23) from Eq. (A.22), the contribution

$$
\Delta L = \overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}} - h(\varphi) \boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ - (1 - h(\varphi)) \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- \tag{A.24}
$$

has to be transformed. Taking into account the chain rule regarding the interpolation of the strain rate

$$
\begin{aligned}
\dot{\overline{\boldsymbol{\varepsilon}}} &= \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi} \boldsymbol{\varepsilon}^+ + h(\varphi) \dot{\boldsymbol{\varepsilon}}^+ - \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi} \boldsymbol{\varepsilon}^- + (1 - h(\varphi)) \dot{\boldsymbol{\varepsilon}}^- \\
&= \left[\!\left[\boldsymbol{\varepsilon}\right]\!\right] \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi} + h(\varphi) \dot{\boldsymbol{\varepsilon}}^+ + (1 - h(\varphi)) \dot{\boldsymbol{\varepsilon}}^-
\end{aligned} \tag{A.25}
$$

the stress power $\overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}}$ is written as

$$
\begin{aligned}
\overline{\boldsymbol{\sigma}} \cdot \dot{\overline{\boldsymbol{\varepsilon}}} = {} & (h(\varphi))^2 \boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ + h(\varphi)(1 - h(\varphi)) \left(\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^- + \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^+ \right) \\
& + (1 - h(\varphi))^2 \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- + \left(h(\varphi) \boldsymbol{\sigma}^+ + (1 - h(\varphi)) \boldsymbol{\sigma}^- \right) \cdot \left[\!\left[\boldsymbol{\varepsilon}\right]\!\right] \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi}
\end{aligned} \tag{A.26}
$$

and Eq. (A.24) reads

$$
\begin{aligned}
\Delta L = {} & h(\varphi) \boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ (h(\varphi) - 1) + (1 - h(\varphi)) \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- (1 - h(\varphi) - 1) \\
& + h(\varphi)(1 - h(\varphi)) \left(\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^- + \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^+ \right) \\
& + \left(h(\varphi) \boldsymbol{\sigma}^+ + (1 - h(\varphi)) \boldsymbol{\sigma}^- \right) \cdot \left[\!\left[\boldsymbol{\varepsilon}\right]\!\right] \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi}
\end{aligned} \tag{A.27}
$$

$$
\begin{aligned}
= {} & h(\varphi) (1 - h(\varphi)) \left(\boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^- + \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^+ - \boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ - \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- \right) \\
& + \left(h(\varphi) \boldsymbol{\sigma}^+ + (1 - h(\varphi)) \boldsymbol{\sigma}^- \right) \cdot \left[\!\left[\boldsymbol{\varepsilon}\right]\!\right] \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi}
\end{aligned} \tag{A.28}
$$

Accounting for

$$
\begin{aligned}
& \boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^- + \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^+ - \boldsymbol{\sigma}^+ \cdot \dot{\boldsymbol{\varepsilon}}^+ - \boldsymbol{\sigma}^- \cdot \dot{\boldsymbol{\varepsilon}}^- \\
& \quad = - \left(\boldsymbol{\sigma}^+ - \boldsymbol{\sigma}^- \right) \cdot \left(\dot{\boldsymbol{\varepsilon}}^+ - \dot{\boldsymbol{\varepsilon}}^- \right) = - \left[\!\left[\boldsymbol{\sigma}\right]\!\right] \cdot \left[\!\left[\dot{\boldsymbol{\varepsilon}}\right]\!\right] \equiv - \left[\!\left[\boldsymbol{\sigma}\right]\!\right] \cdot \left[\!\left[\boldsymbol{D}\right]\!\right] = - \left[\!\left[\boldsymbol{\sigma}\right]\!\right] \cdot \left[\!\left[\boldsymbol{L}\right]\!\right]
\end{aligned} \tag{A.29}
$$

as well as for the Hadamard condition for the velocity gradient $\left[\!\left[\boldsymbol{L}\right]\!\right] = \boldsymbol{d} \otimes \boldsymbol{n}_{\mathcal{S}}$ according to Fosdick and Royer-Carfagni [71]

$$
\left[\!\left[\boldsymbol{\sigma}\right]\!\right] \cdot \left[\!\left[\boldsymbol{L}\right]\!\right] = \left[\!\left[\boldsymbol{\sigma}\right]\!\right] \cdot (\boldsymbol{d} \otimes \boldsymbol{n}_{\mathcal{S}}) = \left[\!\left[\boldsymbol{\sigma} \boldsymbol{n}_{\mathcal{S}}\right]\!\right] \cdot \boldsymbol{d} = \boldsymbol{0} \cdot \boldsymbol{d} = 0 \rightsquigarrow \left[\!\left[\boldsymbol{\sigma}\right]\!\right] \cdot \left[\!\left[\dot{\boldsymbol{\varepsilon}}\right]\!\right] = 0 \tag{A.30}
$$

with $\boldsymbol{d}$ denoting the jump vector associated with $\boldsymbol{L}$ and $\boldsymbol{n}_{\mathcal{S}}$ the normal vector of the singular surface, as well as the symmetry of the Cauchy stress tensor allowing for $\overline{\boldsymbol{\sigma}} \cdot \left[\!\left[\boldsymbol{\varepsilon}\right]\!\right] = \overline{\boldsymbol{\sigma}} \cdot \left[\!\left[\boldsymbol{H}\right]\!\right]$, Eq. (A.28) is given by

$$\Delta L = \left(h(\varphi)\boldsymbol{\sigma}^{+} + (1 - h(\varphi))\boldsymbol{\sigma}^{-}\right) \cdot \left[\!\left[\boldsymbol{H}\right]\!\right] \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi}. \tag{A.31}$$

Moreover, accounting for the Hadamard condition for the displacement gradient $\boldsymbol{H}$ by

$$\left[\!\left[\boldsymbol{F}\right]\!\right] = \boldsymbol{a} \otimes \boldsymbol{n}_{\mathcal{S}}, \quad \left[\!\left[\boldsymbol{F}\right]\!\right] = \left[\!\left[\boldsymbol{H} - \boldsymbol{I}\right]\!\right] = \left[\!\left[\boldsymbol{H}\right]\!\right] \rightsquigarrow \left[\!\left[\boldsymbol{H}\right]\!\right] = \boldsymbol{a} \otimes \boldsymbol{n}_{\mathcal{S}}, \tag{A.32}$$

with $\boldsymbol{a}$ denoting the jump vector associated with $\boldsymbol{\varepsilon}$, the subsequent transformation holds true

$$\begin{aligned}
\overline{\boldsymbol{\sigma}} \cdot \left[\!\left[\boldsymbol{\varepsilon}\right]\!\right] &= \left(h(\varphi)\boldsymbol{\sigma}^{+} + (1 - h(\varphi))\,\boldsymbol{\sigma}^{-}\right) \cdot (\boldsymbol{a} \otimes \boldsymbol{n}_{\mathcal{S}}) \\
&= \left(h(\varphi)\boldsymbol{\sigma}^{+}\boldsymbol{n}_{\mathcal{S}} + (1 - h(\varphi))\,\boldsymbol{\sigma}^{-}\boldsymbol{n}_{\mathcal{S}}\right) \cdot \boldsymbol{a} \\
&= \left(h(\varphi) + (1 - h(\varphi))\right)\left(\boldsymbol{\sigma}^{+}\boldsymbol{n}_{\mathcal{S}}\right) \cdot \boldsymbol{a} \\
&= \left(\boldsymbol{\sigma}^{+}\boldsymbol{n}_{\mathcal{S}}\right) \cdot \left(\left(\boldsymbol{H}^{+} - \boldsymbol{H}^{-}\right)\boldsymbol{n}_{\mathcal{S}}\right) = \left(\boldsymbol{\sigma}^{+}\boldsymbol{n}_{\mathcal{S}}\right) \cdot \left(\left[\!\left[\boldsymbol{H}\right]\!\right]\boldsymbol{n}_{\mathcal{S}}\right),
\end{aligned} \tag{A.33}$$

where $\left[\!\left[\boldsymbol{H}\right]\!\right]\boldsymbol{n}_{\mathcal{S}} = \boldsymbol{a}$ and the balance of linear momentum for a material singular surface are used. Consequently, Eq. (A.31) reads

$$\Delta L = \left(\boldsymbol{\sigma}^{+}\boldsymbol{n}_{\mathcal{S}}\right) \cdot \left(\left[\!\left[\boldsymbol{H}\right]\!\right]\boldsymbol{n}_{\mathcal{S}}\right) \frac{\partial h(\varphi)}{\partial \varphi} \dot{\varphi}. \tag{A.34}$$

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