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Journal Article**Author(s):**

Hütter, Markus

Publication date:

2006-04

Permanent link:

<https://doi.org/10.3929/ethz-b-000024646>

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Originally published in:

Journal of Non-Equilibrium Thermodynamics 31(1), <https://doi.org/10.1515/JNETDY.2006.005>

Volume Change and Non-Local Driving Force in Crystallization

Markus Hütter

ETH-Zürich, Department of Materials, Institute of Polymers, Wolfgang-Pauli-Str.
10, ETH-Hönggerberg HCI H 529, CH-8093 Zürich, Switzerland
(markus.huetter@mat.ethz.ch)

Communicated by B.J. Edwards, Knoxville, USA, and K.H. Hoffmann, Chemnitz, Germany

Abstract

A simplified crystallization model is developed with emphasis on situations of disparate specific volumes of the solid and liquid phases. Using the general equation for the nonequilibrium reversible–irreversible coupling (GENERIC), the model is formulated in terms of the average momentum density, the degree of crystallinity, a single temperature, and a single pressure, where in particular the latter two are appealing for comparison with experiments. In order to describe the volume expansion upon crystallization, a dissipative mass current density is introduced, for which a constitutive relation is derived. One finds that by way of the Onsager–Casimir symmetry, the introduction of this irreversible current also leads to a modification of the driving force for phase change. Rather than depending only on the local chemical potential difference, it also contains a non-local term, namely the Laplacian of the ratio of pressure p to temperature T , multiplied by the square of a screening length. The model is studied for the specific case of aluminum, for which a perturbation analysis is performed. The results show that the type and rate of relaxation of a perturbation depend strongly on its wavelength and on the screening length.

1. Introduction

A general framework for modeling two-phase systems in inhomogeneous situations has been developed in the past, as described in the books by Ishii [1], Nigmatulin [2], and Drew and Passman [3]. In connection to phase

transitions, such models have been used to model alloy solidification [4–6], and also to express the driving force for phase change in terms of the thermodynamic state of the two phases [7, 8]. Here, we discuss the specific situation where the solid and liquid mass densities are different, which amounts to a contraction or expansion of the material due to progressing phase transformation. Let $\rho_s := M_s/V$ and $\rho_l := M_l/V$ denote the extrinsic mass density of the solid and the liquid phase, respectively, i.e., the respective mass divided by the sum of solid and liquid volume, V . The transfer of a certain amount of mass from the liquid to the solid phase due to phase transformation, ΔM , results in a change of the extrinsic mass densities,

$$\Delta\rho_s = \frac{\Delta M}{V} - \rho_s \frac{\Delta V}{V}, \quad (1)$$

$$\Delta\rho_l = -\frac{\Delta M}{V} - \rho_l \frac{\Delta V}{V}. \quad (2)$$

In these equations, the first terms on the right side express the transfer contributions at constant volume. Note that these terms are local in nature, i.e., the solid and liquid contributions cancel locally. The second terms on the right side of the above equations express the expansion of the material. In other words, they describe a flow of matter through the walls of a fixed volume element, and thus we expect that each of these terms is expressed as the divergence of a current density in a continuum description. The corresponding contributions of the solid and liquid phases do not cancel each other locally, rather they vanish only after spatial integration. Furthermore, the first and second terms on the right-hand side should arise only simultaneously, unless the specific volumes of the two phases are identical, in which case the terms proportional to ΔV are absent.

The overall expansion of the volume element can be described in two fundamentally different ways. On the one hand, the volume expansion can be seen as emerging exclusively from a secondary effect: An inhomogeneous rate of phase transformation results in an inhomogeneous pressure modification, which in turn generates an additional contribution to the velocity field by virtue of the momentum balance. On the other hand, this effect can be accompanied by the occurrence of a mass density current that arises simultaneously (rather than as a secondary effect only) with the local phase change contributions, i.e., that this additional current is proportional to the rate of phase transformation. In contrast to current literature, we elaborate on this idea and show the consequences of implementing the phase change-induced dissipative current in a nonequilibrium thermodynamics formalism. While doing so, special attention is also paid to formulating the model in terms

of variables that are closely related to experiment, namely temperature and pressure.

The manuscript is organized as follows. After a brief introduction to the non-equilibrium thermodynamics technique in Section 2, the model is developed in Section 3 and then applied to the crystallization of aluminum in Section 4. The manuscript concludes with a discussion in Section 5.

2. GENERIC formalism

A general equation for the nonequilibrium reversible–irreversible coupling (GENERIC) has been developed for describing nonequilibrium systems [9–11]. It deals with isolated systems, i.e., the total energy is conserved and entropy production is non-negative. The set of independent variables that describe the physics of interest in sufficient detail shall be denoted here by \mathbf{x} , which may have discrete as well as continuous indices. The time evolution of these variables \mathbf{x} is then written in the form

$$\frac{d\mathbf{x}}{dt} = \mathbf{L}(\mathbf{x}) \cdot \frac{\delta E}{\delta \mathbf{x}} + \mathbf{M}(\mathbf{x}) \cdot \frac{\delta S}{\delta \mathbf{x}}, \quad (3)$$

where the two generators E and S are the total energy and entropy functionals, respectively, in terms of the state variables \mathbf{x} ; \mathbf{L} and \mathbf{M} are certain matrices (operators), and \cdot denotes the appropriate inner product. The matrix multiplications imply not only summations over discrete indices but also integration over continuous variables, and $\delta/\delta \mathbf{x}$ typically implies functional rather than partial derivatives (for more details, see [9–11]). The GENERIC structure also imposes certain conditions on the building blocks in Eq. (3). First, Eq. (3) is supplemented by the degeneracy requirements

$$\mathbf{L}(\mathbf{x}) \cdot \frac{\delta S}{\delta \mathbf{x}} = \mathbf{0}, \quad (4)$$

$$\mathbf{M}(\mathbf{x}) \cdot \frac{\delta E}{\delta \mathbf{x}} = \mathbf{0}. \quad (5)$$

The requirement that the (functional) derivative of the entropy lies in the null space of \mathbf{L} represents the reversible nature of \mathbf{L} . On the other hand, the requirement that the functional derivative of the energy lies in the null space of \mathbf{M} manifests that the total energy is not altered by the \mathbf{M} contribution to the dynamics. In addition to these degeneracy requirements, \mathbf{L} must be anti-symmetric and fulfill the Jacobi identity, whereas \mathbf{M} needs to be positive

semi-definite and Onsager–Casimir symmetric. As a result of all these conditions, one may easily show that the GENERIC Eq. (3) implies both the conservation of total energy as well as a nonnegative entropy production. The two contributions to the time evolution of \mathbf{x} generated by the total energy E and the entropy S in Eq. (3) are called the reversible and irreversible contributions, respectively.

3. Model formulation

3.1. Choice of variables

The choice of variables is a crucial step in formulating a model. On the one hand, the set of variables must be sufficient to describe the system and the physics on the level of interest and to the desired detail, and the variables should all be independent of each other. On the other hand, practical applicability of the model sets severe constraints, too. The richness of a detailed model is often lost when switching from formulating the equations to the actual applications, because the number of unknowns is prohibitively large, constitutive equations are missing, or the formulation of boundary conditions is cumbersome.

In order to describe the two-phase system here, the variables consist of the total momentum density \mathbf{u} , a single temperature T , a single pressure p , and the volume fraction, i.e., the degree of crystallinity ϕ , so one has

$$\mathbf{x} = \{\mathbf{u}, T, p, \phi\}. \quad (6)$$

The choice of temperature and pressure is in clear contrast to common practice in non-equilibrium thermodynamics modeling where density variables (mass density and energy or entropy density) are usually used, for which conservation laws can be formulated in a direct manner. The advantages of choosing T and p include a more direct implementation of boundary conditions in contrast to the boundary conditions for, e.g., energy densities. Furthermore, the temperature and pressure are connected directly to the parameters under experimental control, and correspond to the preferred use of the free enthalpy in equilibrium thermodynamics in many applications. However, by using only a single temperature and pressure variable, we implicitly assume that we model the system on time scales on which both quantities are locally equilibrated between the two phases. The choice of a single momentum density (or velocity field) is justified by either neglecting external forces or by assuming infinitely high interfacial friction between the two phases [1]. The set of variables \mathbf{x} gives a simplified, but also more tractable, description

than other two-phase modeling approaches that use two mass densities, two velocity fields, and two internal energy densities (see, e.g., [1–3, 8, 12]). It will become clear below that much of the important physics is captured with the limited set of variables chosen here. It should be mentioned for completeness that turbulent and fluctuating contributions are neglected altogether [1].

The generating functionals for the dynamics in the GENERIC are the total energy E and the entropy S . Here, we assume that the internal energy density e and the entropy density s of the total system consist additively of the corresponding single phase contributions, weighted by the respective volume fraction,

$$E = \int \left[\frac{\mathbf{u}^2}{2\rho} + e \right] d^3r, \quad S = \int s d^3r, \quad (7)$$

with

$$\rho = \rho(p, T, \phi) = \phi \tilde{\rho}_s(p, T) + (1 - \phi) \tilde{\rho}_l(p, T) = \rho_s + \rho_l, \quad (8)$$

$$e = e(p, T, \phi) = \phi \tilde{e}_s(p, T) + (1 - \phi) \tilde{e}_l(p, T) = e_s + e_l, \quad (9)$$

$$s = s(p, T, \phi) = \phi \tilde{s}_s(p, T) + (1 - \phi) \tilde{s}_l(p, T) = s_s + s_l. \quad (10)$$

The quantities $\tilde{\rho}_i$ ($i = s, l$) denote the intrinsic mass densities of phase i with respect to the unit volume of phase i . On the other hand, the extrinsic mass densities are defined as $\rho_s := \phi \tilde{\rho}_s$ and $\rho_l := (1 - \phi) \tilde{\rho}_l$, respectively. The nomenclature for the energy densities (e) and entropy densities (s) is exactly analogous. The functional derivatives of the energy and entropy in Eq. (7) are given by

$$\frac{\delta E}{\delta \mathbf{x}} = \begin{pmatrix} \mathbf{v} \\ -\frac{v^2}{2} \rho_{,T} + e_{,T} \\ -\frac{v^2}{2} \rho_{,p} + e_{,p} \\ -\frac{v^2}{2} \rho_{,\phi} + e_{,\phi} \end{pmatrix}, \quad \frac{\delta S}{\delta \mathbf{x}} = \begin{pmatrix} \mathbf{0} \\ s_{,T} \\ s_{,p} \\ s_{,\phi} \end{pmatrix}, \quad (11)$$

where the velocity \mathbf{v} is defined as \mathbf{u}/ρ . Partial derivatives are represented by a subscript comma followed by the differentiation variable, i.e., $\rho_{,T} = \partial\rho/\partial T$, while it is tacitly assumed that all other variables specified in \mathbf{x} are held constant.

In equilibrium systems, the thermodynamic potential appropriate for the variables temperature and pressure is the free enthalpy. In that respect, it is important to draw attention to the fact that the full thermodynamic information

is contained in the GENERIC treatment given here using T and p , although the generating functionals consist only of the energy and the entropy. The apparent gap to the free enthalpy is closed by the pressure variable itself, by which the remaining thermodynamic information is added and the full information is hence contained.

3.2. Reversible dynamics

In order to determine the reversible dynamics, we now construct the operator \mathbf{L} . It has been discussed and illustrated [10, 11] that this operator is closely related to the generator of space transformations on the field variables. In order to simplify the discussion, we first consider the following ansatz for the dynamic equations themselves. In addition to the usual momentum density balance, the equations of the temperature, pressure, and volume fraction can be written in the general form

$$\partial_t T = -\mathbf{v} \cdot \nabla T - \Omega_T \nabla \cdot \mathbf{v}, \quad (12)$$

$$\partial_t p = -\mathbf{v} \cdot \nabla p - \Omega_p \nabla \cdot \mathbf{v}, \quad (13)$$

$$\partial_t \phi = -\mathbf{v} \cdot \nabla \phi - \Omega_\phi \nabla \cdot \mathbf{v}. \quad (14)$$

The first term on the right-hand side of these equations represents the transport with the flow field. The second term proportional to Ω_T , Ω_p , and Ω_ϕ , respectively, expresses the fact that in general these three variables are neither scalars nor scalar densities, and hence the volumetric terms are not yet determined. Inspection of the energy gradient in Eq. (11) leads to the following proposition for the reversible operator:

$$\mathbf{L} = \begin{pmatrix} -(\nabla \mathbf{u} + \mathbf{u} \nabla)^t & +[\nabla T] - \nabla \Omega_T & +[\nabla p] - \nabla \Omega_p & +[\nabla \phi] - \nabla \Omega_\phi \\ -[\nabla T] - \Omega_T \nabla & 0 & 0 & 0 \\ -[\nabla p] - \Omega_p \nabla & 0 & 0 & 0 \\ -[\nabla \phi] - \Omega_\phi \nabla & 0 & 0 & 0 \end{pmatrix}, \quad (15)$$

with $(\dots)^t$ denoting the transpose with respect to the discrete vector indices. The brackets $[\dots]$ indicate that the action of the derivative operator is restricted to within the brackets, while all other derivative operators act on everything to their right, also on the functions multiplied to the right of the operator \mathbf{L} . The degeneracy requirement for the entropy (4) and conservation of total mass then become (up to additive constants, which we set to zero)

$$[\Omega_{T\mathcal{S},T} + \Omega_{p\mathcal{S},p} + \Omega_{\phi\mathcal{S},\phi}] = s, \quad (16)$$

$$[\Omega_{T\rho,T} + \Omega_{p\rho,p} + \Omega_{\phi\rho,\phi}] = \rho. \quad (17)$$

Note that this Poisson operator is anti-symmetric by construction and satisfies the Jacobi identity [13].

While the two constraints (16) and (17) are necessary consequences of the degeneracy requirement (4), they do not determine the three functions $(\Omega_T, \Omega_p, \Omega_\phi)$ uniquely. In order to do so, a third condition is necessary. Since the discussion in this manuscript targets the various effects on the mass balance equations for the solid and liquid phases, we aim at having the balance equations for the two mass densities ρ_s and ρ_l in the usual form. It can be shown that this is achieved if the condition

$$[\Omega_{T\rho_s,T} + \Omega_{p\rho_s,p} + \Omega_{\phi\rho_s,\phi}] = \rho_s \quad (18)$$

holds in addition to Eqs. (16) and (17).

3.3. Irreversible dynamics: Phase change

3.3.1. Inclusion of volume change effects The irreversible matrix representing the isochore phase change contributions, i.e., the first terms on the right-hand side of Eqs. (1) and (2), has been discussed already previously [7], but for a completely different set of variables. According to [7], the corresponding irreversible matrix, first, does not contain any spatial derivatives, and second, it does not alter the balance equation for the momentum density. Third, the matrix must have rank one because it represents only one single phenomenon, namely the change in the overall degree of crystallinity ϕ . We mention that a separation of nucleation and growth would require the introduction of additional morphological variables (see e.g. [7]). However, such an extension does not alter the discussion on the crystallization-induced volume expansion that we discuss here, and hence such a possible extension is not considered in the following. The symmetric and positive semi-definite matrix is then of the form [7]

$$\mathbf{M}_{\text{pc,iso}} = \mathbf{a} \otimes D\mathbf{a}^T \quad \text{with } \mathbf{a} = \begin{pmatrix} \mathbf{0} \\ \check{T} \\ \check{p} \\ 1 \end{pmatrix}, \quad (19)$$

with a rate coefficient $D \geq 0$. The functions \check{T} and \check{p} represent the change in temperature and pressure, respectively, proportional to the isochore

change in the volume fraction due to phase change,

$$\dot{\phi}|_{\text{pc,iso}} \equiv D\mathbf{a}^T \cdot \delta S / \delta \mathbf{x}.$$

In other words, one can show by calculating

$$\mathbf{M}_{\text{pc,iso}} \cdot \delta S / \delta \mathbf{x} \quad \text{that} \quad \dot{T}|_{\text{pc,iso}} = \check{T}\dot{\phi}|_{\text{pc,iso}} \quad \text{and} \quad \dot{p}|_{\text{pc,iso}} = \check{p}\dot{\phi}|_{\text{pc,iso}}.$$

Requiring $\mathbf{M}_{\text{pc,iso}}$ to be independent of the velocity \mathbf{v} together with the degeneracy requirement (5) and the energy functional (7) leads to the conditions

$$\check{T}\rho_{,T} + \check{p}\rho_{,p} + \rho_{,\phi} = 0, \quad (20)$$

$$\check{T}e_{,T} + \check{p}e_{,p} + e_{,\phi} = 0. \quad (21)$$

Note that Eq. (20) respects the conservation of total mass $\mathcal{M} := \int \rho d^3r$, i.e., one has

$$\mathbf{M}_{\text{pc,iso}} \cdot \delta \mathcal{M} / \delta \mathbf{x} = \mathbf{0}.$$

The restriction to formulate the phase change contribution in purely local terms is unnecessary. In the following, we study the effect of implementing non-local contributions, guided by the discussion given in the Introduction. For the contribution representing volume change (second terms on the right-hand side of Eqs. (1) and (2)), we first derive a diffusive current \mathbf{j}_{pc} in the total mass balance equation due to phase change, which is proportional to the total mass density ρ as suggested by Eqs. (1) and (2), $\mathbf{j}_{\text{pc}} = \rho \mathbf{v}_{\text{pc}}$. The balance equation for the total mass density thus has an irreversible contribution of the form

$$-\nabla \cdot \mathbf{j}_{\text{pc}} = -(\nabla \rho) \cdot \mathbf{v}_{\text{pc}} - \rho \nabla \cdot \mathbf{v}_{\text{pc}}. \quad (22)$$

With the aid of $\rho(T, p, \phi)$, Eq. (22) will be represented by contributions of the form $\mathbf{v}_{\text{pc}} \cdot \nabla$ and $(\nabla \cdot \mathbf{v}_{\text{pc}})$ in the equations for the temperature, pressure and volume fraction, respectively.

For including the effect of the dissipative current \mathbf{j}_{pc} into the dynamic equations by means of a modification of the dissipative matrix (19), we use the following criteria. The dissipative current \mathbf{j}_{pc} must come into existence simultaneously with the isochore phase change contribution, as discussed in the Introduction. Therefore, rather than introducing an additive term to the entire matrix \mathbf{M} , we add the non-isochore terms into the vector \mathbf{a} in Eq. (19). In so doing, the matrix that mimics the isochore and the non-isochore terms simultaneously still has rank one by construction, in agreement with originating

from the same single phenomenon, namely crystallization. Then, in order to represent the effect of \mathbf{v}_{pc} appropriately as discussed after Eq. (22), we add terms of the form $-(\llbracket \nabla T \rrbracket + \bar{\Omega}_T \nabla)$, $-(\llbracket \nabla p \rrbracket + \bar{\Omega}_p \nabla)$, and $-(\llbracket \nabla \phi \rrbracket + \bar{\Omega}_\phi \nabla)$, to the temperature, pressure and volume fraction components of the vector \mathbf{a} , respectively, with the condition

$$\bar{\Omega}_T \rho_{,T} + \bar{\Omega}_p \rho_{,p} + \bar{\Omega}_\phi \rho_{,\phi} = \rho. \quad (23)$$

If these terms added to the components of \mathbf{a} are multiplied by \mathbf{v}_{pc} from the right, the contributions in Eq. (22) are recovered by virtue of the chain rule and Eq. (23). In analogy to the functions $(\Omega_T, \Omega_p, \Omega_\phi)$ in Eqs. (12)–(14), the functions $(\bar{\Omega}_T, \bar{\Omega}_p, \bar{\Omega}_\phi)$ are needed to take into account possible effects in the dynamic equations for (T, p, ϕ) due to $\nabla \cdot \mathbf{v}_{pc} \neq 0$. Above, $\llbracket \dots \rrbracket$ again denotes action of the derivative operator exclusively inside of the brackets.

In order for the rank of \mathbf{M}_{pc} to be equal to one, the vector-type additions to the components of \mathbf{a} , e.g., $-(\llbracket \nabla T \rrbracket + \bar{\Omega}_T \nabla)$, cannot be contracted with another vector on the other side of the \otimes multiplication sign in Eq. (19), and therefore they are contracted with a vector \mathbf{b} within \mathbf{a} itself, so that \mathbf{a} in Eq. (19) takes the form

$$\mathbf{a} = \begin{pmatrix} \overset{\star}{\check{T}} - (\llbracket \nabla T \rrbracket + \bar{\Omega}_T \nabla) \cdot \mathbf{b} \\ \check{p} - (\llbracket \nabla p \rrbracket + \bar{\Omega}_p \nabla) \cdot \mathbf{b} \\ 1 - (\llbracket \nabla \phi \rrbracket + \bar{\Omega}_\phi \nabla) \cdot \mathbf{b} \end{pmatrix}. \quad (24)$$

The star in the \mathbf{u} component indicates an undetermined element. By inspection of the form of \mathbf{M}_{pc} in Eq. (19), we can already anticipate that the phase change-induced velocity will be given by the expression $\mathbf{v}_{pc} = \mathbf{b} D(\mathbf{a}^T \cdot \delta S / \delta \mathbf{x})$. To determine the vector \mathbf{b} , we note that the only vectors in the present formulation are \mathbf{v} and ∇ . Choosing \mathbf{b} proportional to \mathbf{v} would mean that the driving force for phase change, $\mathbf{a}^T \cdot \delta S / \delta \mathbf{x}$, depends on odd powers of the velocity field, which is clearly not desirable. Therefore, we choose $\mathbf{b} = \lambda_1 \nabla \lambda_2$, where the functions λ_1 and λ_2 in general depend on space coordinates. The same vector \mathbf{b} (i.e., the same functions λ_1 and λ_2) is taken in all components of \mathbf{a} , because all three variables (T, p, ϕ) in combination give rise to the diffusive fluxes in the mass density we are looking for. Since \mathbf{a} now contains spatial derivatives, it is essential to note that \mathbf{a}^T denotes the adjoint operator of \mathbf{a} , rather than simply its vector-transpose, in contrast to the notation used in Eq. (15).

In summary, we find that the modification of the irreversible matrix is of the form

$$\mathbf{M}_{\text{pc}} = \begin{pmatrix} -\nabla_i \mathbf{u} \lambda_1 \nabla_i \lambda_2 \\ \check{T} - ([\nabla T] + \bar{\Omega}_T \nabla) \cdot \lambda_1 \nabla \lambda_2 \\ \check{p} - ([\nabla p] + \bar{\Omega}_p \nabla) \cdot \lambda_1 \nabla \lambda_2 \\ 1 - ([\nabla \phi] + \bar{\Omega}_\phi \nabla) \cdot \lambda_1 \nabla \lambda_2 \end{pmatrix} \otimes D \begin{pmatrix} -\lambda_2 \nabla_j \lambda_1 \mathbf{u} \nabla_j \\ \check{T} + \lambda_2 \nabla \lambda_1 \cdot ([\nabla T] - \nabla \bar{\Omega}_T) \\ \check{p} + \lambda_2 \nabla \lambda_1 \cdot ([\nabla p] - \nabla \bar{\Omega}_p) \\ 1 + \lambda_2 \nabla \lambda_1 \cdot ([\nabla \phi] - \nabla \bar{\Omega}_\phi) \end{pmatrix}. \quad (25)$$

The \mathbf{u} component has been added in order to enable the satisfaction of the degeneracy requirement (5), which turns into Eq. (23) and

$$\bar{\Omega}_T e_{,T} + \bar{\Omega}_p e_{,p} + \bar{\Omega}_\phi e_{,\phi} = e. \quad (26)$$

These degeneracy requirements also ensure the conservation of the total mass. The fact that the degeneracy requirement (5) for a matrix of rank one splits into two conditions, Eqs. (23) and (26), originates from the aim to keep the functions $(\bar{\Omega}_T, \bar{\Omega}_p, \bar{\Omega}_\phi)$ independent of the velocity field \mathbf{v} . It is noteworthy that the constraints (23), (26) for the functions $(\bar{\Omega}_T, \bar{\Omega}_p, \bar{\Omega}_\phi)$ are different from the constraints (16), (17) for the functions $(\Omega_T, \Omega_p, \Omega_\phi)$, which will be discussed in further detail below. The metric matrix (25) is symmetric and positive semi-definite by construction, and is hence a valid extension of Eq. (19) within the GENERIC framework.

3.3.2. Non-local driving force and screening length The driving force for phase transformation, A , can be calculated from Eq. (25). One finds that A consists of an isochore (A_{iso}) and a non-isochore ($A_{\text{non-iso}}$) contribution, in analogy to the first and second terms on the right-hand side of Eqs. (1) and (2), respectively,

$$A = \mathbf{a}^T \cdot \frac{\delta S}{\delta \mathbf{x}} = A_{\text{iso}} + A_{\text{non-iso}}, \quad (27)$$

$$A_{\text{iso}} = \frac{\mu_l - \mu_s}{T} \check{\rho}, \quad (28)$$

$$A_{\text{non-iso}} = \lambda_2 \nabla \cdot \lambda_1 \nabla \left(\frac{p}{T} + \frac{\mu_l - \mu_s}{T} (\rho_s - \bar{\rho}_s) \right), \quad (29)$$

with μ_l and μ_s the chemical potential of the liquid and the solid phase, respectively, and

$$\check{\rho} := \check{T} \rho_{s,T} + \check{p} \rho_{s,p} + \rho_{s,\phi} = -(\check{T} \rho_{l,T} + \check{p} \rho_{l,p} + \rho_{l,\phi}), \quad (30)$$

$$\bar{\rho}_s := \bar{\Omega}_T \rho_{s,T} + \bar{\Omega}_p \rho_{s,p} + \bar{\Omega}_\phi \rho_{s,\phi}. \quad (31)$$

Although we primarily aimed at expressing the effect of volume change through a dissipative mass current \mathbf{j}_{pc} , we find that the driving force for phase change is altered. Similarly, as the volume expansion is inherently a non-local phenomenon, the driving force gets a non-local contribution, $A_{\text{non-iso}}$. This symmetric occurrence of non-locality in terms of the current \mathbf{j}_{pc} and an additional contribution to the driving force, $A_{\text{non-iso}}$, is a direct consequence of the symmetry property of the metric matrix \mathbf{M}_{pc} .

It is essential to note the fundamental difference between Eq. (30) and Eq. (31). On the one hand, $\check{\rho}$ is uniquely determined because the two functions T and \check{p} are uniquely determined by the two constraints (20) and (21). On the other hand, the quantity $\bar{\rho}_s$ simply represents the solid phase contribution to the left-hand side of the condition (23). At this stage $\bar{\rho}_s$ is undetermined because the three functions ($\bar{\Omega}_T, \bar{\Omega}_p, \bar{\Omega}_\phi$) are subject to two constraints only, Eqs. (23) and (26). In order to get an impression of the significance of $\bar{\rho}_s$, we consider the phase change contributions to the mass balance equations for the solid and liquid mass densities, respectively, from $\mathbf{M}_{\text{pc}} \cdot \delta S / \delta \mathbf{x}$:

$$\partial_t \rho_s|_{\text{pc}} = \check{\rho} DA - \nabla \cdot (\rho_s \mathbf{v}_{\text{pc}}) + (\rho_s - \bar{\rho}_s) \nabla \cdot \mathbf{v}_{\text{pc}}, \quad (32)$$

$$\partial_t \rho_l|_{\text{pc}} = -\check{\rho} DA - \nabla \cdot (\rho_l \mathbf{v}_{\text{pc}}) - (\rho_s - \bar{\rho}_s) \nabla \cdot \mathbf{v}_{\text{pc}}, \quad (33)$$

with the velocity field induced by the phase change

$$\mathbf{v}_{\text{pc}} := \lambda_1 \nabla (\lambda_2 DA). \quad (34)$$

One observes that only for $\bar{\rho}_s = \rho_s$, the non-isochore terms can be written as the divergence of the current $\mathbf{j}_{s,\text{pc}} = \rho_s \mathbf{v}_{\text{pc}}$ and $\mathbf{j}_{l,\text{pc}} = \rho_l \mathbf{v}_{\text{pc}}$, respectively, which closely mimics the second terms on the right-hand side of Eqs. (1) and (2). Therefore, we will use $\bar{\rho}_s = \rho_s$ throughout the remainder of this manuscript. At this point, it is also noted that the two balance equations (32), (33) demonstrate that $A > 0$ stands for crystallization, while $A < 0$ represents melting conditions.

The expression for the non-isochore contribution to the driving force A simplifies considerably when inserting $\bar{\rho}_s = \rho_s$,

$$A_{\text{non-iso}} = \lambda_2 \nabla \cdot \lambda_1 \nabla \frac{p}{T}. \quad (35)$$

A dimensional analysis of the components of Eq. (25) shows that the product $\lambda_1 \lambda_2$ has the dimension $(\text{length})^2$. The individual meaning of the two functions is unknown, and so further discussion must be based on physical intuition.

In the following, we interpret the consequences of choosing $\lambda_1 = 1$, which has ramifications for both the induced velocity field \mathbf{v}_{pc} , Eq. (34), and for the driving force A , Eq. (35). It can be shown by using a Taylor expansion of p/T that the quantity $\lambda_2 \nabla \cdot \nabla(p/T)$ measures the difference between the value of p/T at the local position and a spherically symmetric average of p/T in the vicinity with a radius of the order $\sqrt{|\lambda_2|}$. The significance of the non-isochore contribution $A_{\text{non-iso}}$ is then the following: The first part of the driving force, A_{iso} , is purely local. It checks the local thermodynamic feasibility for a possible phase transition by comparing the chemical potentials. If the solid state is thermodynamically favorable, the system is driven into the solid state. The second part, $A_{\text{non-iso}}$, works similarly in the sense that it checks whether the pressure conditions are favorable for volume expansion or contraction. In more detail, this term screens the λ_2 vicinity and checks whether at this point there is local minimum or maximum of p/T . Only the sum of the local and the non-local contribution decides whether and in what direction the phase change will take place.

Let us discuss in more detail how the non-isochore term actually acts. The isochore term A_{iso} shows the homogeneous driving force for crystallization, negative values indicate melting. In order to simplify the discussion of the non-isochore term $A_{\text{non-iso}}$, it is assumed in the following that the temperature field does not depend on the position. We compare the situation of a spatially constant pressure p_0 to a pressure field $p_{\text{min}}(\mathbf{r})$ that has a local minimum at \mathbf{r}_0 with $p_{\text{min}}(\mathbf{r}_0) = p_0$. If the phase transformation were to lead to an increase in the specific volume of the two-phase system, this volume expansion would be hindered more so for the pressure profile $p_{\text{min}}(\mathbf{r})$ than for the constant pressure p_0 . For $\tilde{\rho}_s > \tilde{\rho}_l$ volume expansion due to phase change arises due to melting, i.e., $A < 0$, and therefore the requirement of a decreased driving force for melting, $0 > A[p_{\text{min}}(\mathbf{r})] > A[p_0]$, translates into $A_{\text{non-iso}}[p_{\text{min}}(\mathbf{r})] > 0$, by virtue of the condition $p_{\text{min}}(\mathbf{r}_0) = p_0$. Since the local curvature of the pressure profile $p_{\text{min}}(\mathbf{r})$ is positive, one concludes that $\lambda_2 > 0$. A discussion of the velocity field \mathbf{v}_{pc} leads to the same conclusion. On the other hand, if the solid phase is less dense than the liquid phase (e.g., ice), a similar argument as above results in $\lambda_2 < 0$. Furthermore, we point out that the velocity \mathbf{v}_{pc} should vanish if the solid and liquid mass densities are equal.

In summary, all these different scenarios for inhomogeneous crystallization conditions can be captured in a qualitative way by writing

$$\lambda_2 = N_0^2(\xi_l^2 - \xi_s^2), \quad (36)$$

with the characteristic length scales of the solid and liquid phase, respectively,

$$\xi_s := \sqrt[3]{M_0/\bar{\rho}_s}, \quad (37)$$

$$\xi_l := \sqrt[3]{M_0/\bar{\rho}_l}, \quad (38)$$

with M_0 the mass of a crystallizing unit. For low molecular weight systems, such as metals, this crystallizing unit is a single molecule, while for polymers, the unit is a fraction of the entanglement molecular weight (similar to what is usually denoted as “stem”). The quantity N_0 determines over how many unit lengths the vicinity is scanned for the pressure comparison in the driving force A .

Note that for this model to prevent under- or overshooting in the degree of crystallinity ($\phi < 0$ or $\phi > 1$), the kinetic prefactor D should obey $\lim_{\phi \rightarrow 0} D = 0$ and $\lim_{\phi \rightarrow 1} D = 0$. A possible choice to achieve that is $D \propto \phi^{k_1}(1-\phi)^{k_2}$ ($k_1, k_2 > 0$), or the Nakamura form $D \propto m(1-\phi)[- \ln(1-\phi)]^{1-1/m}$ with $m > 1$, [14, 15].

3.4. The complete model

The dynamic equations of the variables \mathbf{x} contain not only reversible and phase change contributions, but viscous stress and thermal conduction are also important in real systems. Since the focus in this manuscript is not on these effects, they are incorporated simply by generalizing their corresponding single phase formulations. In order to keep the main part of the manuscript straightforward, the reader is referred to the Appendix for their derivation.

The full set of dynamic equations is obtained by the action of the reversible operator (15) and the irreversible operators (25), (77) on the functional derivatives (11), with the result

$$\partial_t \mathbf{u} = -\nabla \cdot ((\mathbf{v} + \mathbf{v}_{pc})\mathbf{u}) - \nabla \cdot (p\mathbf{1} + \boldsymbol{\tau}), \quad (39)$$

$$D_t T = -\Omega_T(\nabla \cdot \mathbf{v}) - \bar{\Omega}_T(\nabla \cdot \mathbf{v}_{pc}) + \check{T}DA - \Omega_T^{\eta, \lambda_{th}}(\boldsymbol{\tau} : (\nabla \mathbf{v})^T + \nabla \cdot \mathbf{j}_q), \quad (40)$$

$$D_t p = -\Omega_p(\nabla \cdot \mathbf{v}) - \bar{\Omega}_p(\nabla \cdot \mathbf{v}_{pc}) + \check{p}DA - \Omega_p^{\eta, \lambda_{th}}(\boldsymbol{\tau} : (\nabla \mathbf{v})^T + \nabla \cdot \mathbf{j}_q), \quad (41)$$

$$D_t \phi = -\Omega_\phi(\nabla \cdot \mathbf{v}) - \bar{\Omega}_\phi(\nabla \cdot \mathbf{v}_{pc}) + DA - \Omega_\phi^{\eta, \lambda_{th}}(\boldsymbol{\tau} : (\nabla \mathbf{v})^T + \nabla \cdot \mathbf{j}_q), \quad (42)$$

where we have used the abbreviation $D_t \equiv \partial_t + (\mathbf{v} + \mathbf{v}_{pc}) \cdot \nabla$ for the material derivative. In the reversible contributions, the functions ($\Omega_T, \Omega_p, \Omega_\phi$) are determined by the constraints (16)–(18). The thermodynamic driving force A is given by Eq. (27), with the isochore and non-isochore contributions Eqs. (28), (30) and Eq. (35) with $\lambda_1 = 1$, respectively, and the velocity

field \mathbf{v}_{pc} is specified by Eq. (34) with $\lambda_1 = 1$. The functions $(\bar{\Omega}_T, \bar{\Omega}_p, \bar{\Omega}_\phi)$ are given by Eqs. (23), (26) and Eq. (31) with $\bar{\rho}_s = \rho_s$, and \bar{T} and \bar{p} are defined through Eqs. (20) and (21). Finally, the dissipative contributions due to viscous flow and heat conduction are specified through $(\Omega_T^{\eta, \lambda_{\text{th}}}, \Omega_p^{\eta, \lambda_{\text{th}}}, \Omega_\phi^{\eta, \lambda_{\text{th}}})$ given in Eqs. (80)–(82), and $\boldsymbol{\tau}$ and \mathbf{j}_q are the viscous pressure tensor and the heat flux given in Eq. (83) and Eq. (84), respectively. We mention that the momentum balance equation (39) can be written in the form

$$D_t \mathbf{v} = -\frac{1}{\rho} \nabla \cdot (p \mathbf{1} + \boldsymbol{\tau}), \quad (43)$$

where we have used that, by virtue of the above conditions, the total mass density obeys a balance equation in the usual form with the mass transport velocity $\mathbf{v} + \mathbf{v}_{\text{pc}}$.

Owing to the conditions mentioned above, the eleven functions $\Omega_\star, \bar{\Omega}_\star, \Omega_\star^{\eta, \lambda_{\text{th}}}$ ($\star = T, p, \phi$), \bar{T} and \bar{p} are uniquely defined. After a lengthy but straightforward calculation, one gets

$$\Omega_T = \frac{T \langle \alpha \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (44)$$

$$\Omega_p = \frac{\langle c_p \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (45)$$

$$\Omega_\phi = -\phi(1 - \phi) \frac{(\kappa_s - \kappa_l) \langle c_p \rangle - (\alpha_s - \alpha_l) T \langle \alpha \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (46)$$

$$\bar{\Omega}_T = \frac{T \langle \alpha \rangle - p \langle \kappa \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (47)$$

$$\bar{\Omega}_p = \frac{\langle c_p \rangle - p \langle \alpha \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (48)$$

$$\bar{\Omega}_\phi = -\phi(1 - \phi) \frac{(\kappa_s - \kappa_l) \langle c_p \rangle + p(\alpha_s \kappa_l - \alpha_l \kappa_s) - (\alpha_s - \alpha_l) T \langle \alpha \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (49)$$

$$\Omega_T^{\eta, \lambda_{\text{th}}} = \frac{\langle \kappa \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (50)$$

$$\Omega_p^{\eta, \lambda_{\text{th}}} = \frac{\langle \alpha \rangle}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (51)$$

$$\Omega_\phi^{\eta, \lambda_{\text{th}}} = \phi(1 - \phi) \frac{\alpha_s \kappa_l - \alpha_l \kappa_s}{\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2}, \quad (52)$$

$$\check{T} = \frac{1}{B} [(\tilde{\rho}_s - \tilde{\rho}_l)(p \langle \kappa \rangle - T \langle \alpha \rangle) + \langle \kappa \rangle (\tilde{\rho}_s \tilde{e}_l - \tilde{\rho}_l \tilde{e}_s)], \quad (53)$$

$$\check{p} = \frac{1}{B} [(\tilde{\rho}_s - \tilde{\rho}_l)(p \langle \alpha \rangle - \langle c_p \rangle) + \langle \alpha \rangle (\tilde{\rho}_s \tilde{e}_l - \tilde{\rho}_l \tilde{e}_s)], \quad (54)$$

$$B = -\langle \alpha \tilde{\rho} \rangle T \langle \alpha \rangle + \langle \kappa \tilde{\rho} \rangle \langle c_p \rangle \\ + \phi(1 - \phi) [\tilde{\rho}_s (\tilde{e}_l + p) - \tilde{\rho}_l (\tilde{e}_s + p)] [\alpha_s \kappa_l - \alpha_l \kappa_s], \quad (55)$$

where $\langle Z \rangle := \phi Z_s + (1 - \phi) Z_l$ denotes the volume fraction average of the material properties Z_i ($i = s, l$), with α_i the thermal expansion coefficient of phase i , κ_i the isothermal compressibility of phase i , and c_{pi} the constant pressure heat capacity of phase i per unit volume of phase i . If one uses the expressions (53)–(55) in Eq. (30), one finds the following result for \check{p} :

$$\check{p} = \frac{\tilde{\rho}_s \tilde{\rho}_l}{B} (\langle c_p \rangle \langle \kappa \rangle - T \langle \alpha \rangle^2), \quad (56)$$

which is obviously symmetric with respect to the two phases. In contrast to previous two-phase models [7, 8], the function \check{p} used in the driving force (28) is completely determined. Since we assumed equal temperature and pressure in both phases, the low number of thermodynamic variables (T and p) together with the degeneracy conditions (20), (21) leads to uniquely determined functions \check{T} and \check{p} , and by virtue of Eq. (30) \check{p} is also uniquely determined.

On the basis of Eqs. (39)–(42), one can derive the balance equations for the extrinsic mass densities. The reader should recall that in addition to the constraints imposed by the GENERIC structure, we have imposed the constraints Eq. (18), Eq. (31) with $\bar{\rho}_s = \rho_s$, and Eq. (82). Owing to these three additional constraints, one gets the expected result for the individual mass balance equations, namely Eqs. (32) and (33), in which the interpretation of $\mathbf{v} + \mathbf{v}_{\text{pc}}$ as a transport velocity becomes apparent.

In view of the difference between \mathbf{v} and $\mathbf{v} + \mathbf{v}_{\text{pc}}$ it is particularly interesting to look at the energy equation. Using the degeneracy requirements (16)–(18) one can show that $\Omega_{T e, T} + \Omega_{p e, p} + \Omega_{\phi e, \phi} = e + p$, and thus one finds with Eqs. (39)–(42) for the internal energy balance

$$\partial_t e = -\nabla \cdot ((\mathbf{v} + \mathbf{v}_{\text{pc}})e) - (p\mathbf{1} + \boldsymbol{\tau}) : (\nabla \mathbf{v})^T - \nabla \cdot \mathbf{j}_q. \quad (57)$$

While $\mathbf{v} + \mathbf{v}_{\text{pc}}$ is the transport velocity of the internal energy density, the velocity field \mathbf{v} appears in the work term, $-(p\mathbf{1} + \boldsymbol{\tau}) : (\nabla\mathbf{v})^T$. This exemplifies the difference between \mathbf{v} , with which the volume change can be expressed as $\nabla \cdot \mathbf{v}$, and $\mathbf{v} + \mathbf{v}_{\text{pc}}$, which is a transport velocity and includes the effect of a dissipative flux. A similar difference between a mass velocity and a volume velocity has been studied in great detail by Brenner [16–18], and was confirmed by nonequilibrium thermodynamics considerations (see p. 61 in [11]). There, it is shown that the difference between the two velocities can be expressed through gradient terms and hence it is relevant for inhomogeneous situations. Furthermore, Brenner points out that, in our nomenclature, the velocity field \mathbf{v} should be used in Newton's expression for the stress tensor, rather than the transport velocity $\mathbf{v} + \mathbf{v}_{\text{pc}}$. This justifies the treatment of the viscous stresses given in the Appendix.

The significance of the transport velocity $\mathbf{v} + \mathbf{v}_{\text{pc}}$ becomes apparent also when using Reynold's transport theorem. For example, let us study the change in the integral internal energy of a given amount of matter, U , contained within a volume $V(t)$. The well-known equation

$$\frac{dU(t)}{dt} = \int_{V(t)} (-(p\mathbf{1} + \boldsymbol{\tau}) : (\nabla\mathbf{v})^T - \nabla \cdot \mathbf{j}_q) dV \quad (58)$$

is obtained from Eq. (57) only if the boundary $\partial V(t)$ moves with the transport velocity $\mathbf{v} + \mathbf{v}_{\text{pc}}$ evaluated at the boundary.

While the isochore contributions cancel in the total internal energy balance equation (57) and hence also in Eq. (58), they appear in the usual form when writing the energy equation in terms of temperature and pressure. From Eqs. (40) and (41) one can show that

$$\langle c_p \rangle D_t T - T \langle \alpha \rangle D_t p = p(\nabla \cdot \mathbf{v}_{\text{pc}}) + \check{\rho} DA \left[\left(\mu_l + T \frac{\check{s}_l}{\check{\rho}_l} \right) - \left(\mu_s + T \frac{\check{s}_s}{\check{\rho}_s} \right) \right]. \quad (59)$$

The expression in the bracket on the right-hand side is the difference in enthalpies per unit mass, i.e., the latent heat.

The modifications \mathbf{v}_{pc} and $A_{\text{non-iso}}$ of the above model with respect to previous models for phase change are relevant in inhomogeneous situations. However, due to the dissipative thermal conduction and viscous stresses, an isolated system becomes homogeneous after a sufficiently long time. Therefore, transient situations or inhomogeneous boundary conditions need to be considered in order to examine the effects of \mathbf{v}_{pc} and $A_{\text{non-iso}}$, as demonstrated below.

4. Application to aluminum

4.1. Material parameters

In this section, we apply the model developed above to the melting/crystallization of aluminum. Two classes of information are required, namely the thermodynamic properties and the transport coefficients.

The thermodynamic information in terms of the variables T and p is captured by the chemical potential, which should be known at least around a reference state, (T_0, p_0) . If one assumes that the isobaric expansion coefficient and the isothermal compressibility are constant over the range of interest, i.e., $\alpha = \alpha_0$ and $\kappa = \kappa_0$, and if the constant pressure heat capacity per unit mass at (T_0, p_0) is denoted by $\hat{c}_{p,0}$, the chemical potential in the vicinity of (T_0, p_0) is given by

$$\mu(T, p) = \frac{1}{\kappa} \hat{v}_0 e^{\alpha(T-T_0)} [1 - e^{-\kappa(p-p_0)}] + \hat{c}_{p,0} T \left[1 - \ln\left(\frac{T}{T^*}\right) \right] + \hat{\mu}_0, \quad (60)$$

with \hat{v}_0 the specific volume at (T_0, p_0) .

The material parameters of aluminum used in the simulations are given in Table 1. The constants $\hat{\mu}_0$ and T^* characterize the offset in internal energy per unit mass, \hat{e} , and entropy per unit mass, \hat{s} , since it can be shown that

$$\hat{e}(T_0, p_0) = \hat{c}_{p,0} T_0 - p_0 \hat{v}_0 + \hat{\mu}_0, \quad (61)$$

$$\hat{s}(T_0, p_0) = \hat{c}_{p,0} \ln\left(\frac{T_0}{T^*}\right), \quad (62)$$

with two parameters, $\hat{\mu}_0$ and T^* , for each phase that are undetermined so far.

In order to decrease the number of unknowns in Eqs. (61) and (62) for the solid and liquid phases, one can equate the chemical potentials of the solid and liquid phases at two different state points on the melting line.

Table 1 Experimental values for aluminum taken for the simulation with the reference state on the melting line, $T_0 = 933$ K and $p_0 = 10^5$ Pa, including references: isobaric expansion coefficient α , isothermal compressibility κ , specific volume \hat{v}_0 , constant pressure heat capacity per unit mass $\hat{c}_{p,0}$, viscosity η , and thermal conductivity λ_{th} .

Phase	α [K ⁻¹]	κ [Pa ⁻¹]	\hat{v}_0 [m ³ kg ⁻¹]	$\hat{c}_{p,0}$ [JK ⁻¹ kg ⁻¹]	η [Pas]	λ_{th} [Js ⁻¹ m ⁻¹ K ⁻¹]
solid	0.000108 [19]	$1.91 \cdot 10^{-11}$ [20]	0.000391 [21]	1175.9 [22]	–	209.4 [19]
liquid	0.000116 [19]	$2.35 \cdot 10^{-11}$ [20]	0.000422 [19]	1257.4 [22]	0.0012 [23]	90.7 [19]

The latter runs through $T_0 = 933$ K and $p_0 = 10^5$ Pa and has a slope of $dT_m/dp = 65 * 10^{-9}$ K/Pa for aluminum [24]. This reduces the number of unknowns by two. The two remaining parameters capture the freedom to shift the energies per unit mass \hat{e}_s and \hat{e}_l simultaneously, and to shift the entropies per unit mass \hat{s}_s and \hat{s}_l simultaneously. Making a shift $\hat{e}_s \rightarrow \hat{e}_s + \hat{e}_0$ and $\hat{e}_l \rightarrow \hat{e}_l + \hat{e}_0$ adds a term of the form $\hat{e}_0 \int \rho d^3r$ to the total energy functional Eq. (7). However, since the reversible operator \mathbf{L} and all contributions to the irreversible operator \mathbf{M} are degenerate with respect to the gradient of total mass, such an energy shift does not affect the dynamic equations. This can also be seen by looking directly at the final equations (39)–(42) with the definitions (44)–(55). A completely analogous argument holds for the common shift in the entropies per unit mass \hat{s}_s and \hat{s}_l . In conclusion, the only undetermined parameters are the common offset in the energies per unit mass of the two phases, and the common offset in the entropies per unit mass of the two phases, but as we have just shown they are without consequences for the dynamic equations.

In addition to the thermodynamic information, four properties occurring in the dissipative dynamics need to be specified to make the model complete. First, the viscosity and the thermal conductivity values are given in Table 1. The thermal conductivity of the two-phase system can be approximated by the average according to volume fractions of the thermal conductivities of the individual phases, while the viscosity can be approximated using the Krieger–Dougherty relation [25, 26]

$$\eta(\phi) = \eta_l \left(1 - \frac{\phi}{\phi_{\max}} \right)^{-(5/2)\phi_{\max}}, \quad (63)$$

with $\phi_{\max} = 0.637$ for random packing of spherical crystals, and η_l the viscosity of the liquid phase. Because of a lack of experimental data, the magnitude of the bulk viscosity κ_v of aluminum was inferred from data on elements that are close to aluminum in the periodic table [27]. In this study, we have used $\kappa_v = 1.8\eta$.

The two remaining parameters D and λ_2 concern the phase change dynamics. The rate of phase transformation D is obtained by equating $\dot{\phi}|_{\text{pc,iso}} = DA_{\text{iso}}$ for a super-cooling of $\Delta T = 1$ K with experimental data for the same super-cooling. Since in most common aluminum melts, crystallization occurs from heterogeneous nucleation, we have used a crystal density of $n = 10^{11}$ m⁻³ [28] as a first approximation. The experimental rate of crystallization can then be estimated by calculating $\dot{\phi}_A(t_{1/2})$ with the half-time $t_{1/2}$ defined as $\phi_A(t_{1/2}) = 1/2$, where ϕ_A is the degree of crystallinity as derived in the Avrami model [29] with radial crystal growth rate G . With $G = c\Delta T$ with

$c = 0.0418 \text{ ms}^{-1}\text{K}^{-1}$ [30] and assuming three-dimensional growth, one gets a value of $D(\phi = 1/2) = 0.293 \text{ m}^3\text{KJ}^{-1}\text{s}^{-1}$, which is used in the following. Last but not least, we need to determine the measure for the screening length, λ_2 . In order to examine the effect of λ_2 , it shall be taken as a parameter and its influence will be studied in the following.

4.2. Influence of non-local term on driving force

The influence of the non-local term $A_{\text{non-iso}}$ on the total driving force A is now examined. Consider a homogeneous situation, and impose a small perturbation in the pressure at a position \mathbf{r} and in a small vicinity thereof, where the perturbation has an extremum at \mathbf{r} . If the pressure is perturbed, both the local contribution, A_{iso} , and the non-local contribution to the driving force, $A_{\text{non-iso}}$, change at \mathbf{r} with respect to the homogeneous situation. One can show that both terms change in different directions, and thus it is interesting to estimate the overall effect of a local pressure perturbation. We assume for simplicity that the non-local contribution $\lambda_2 \nabla \cdot \nabla p$ evaluated at \mathbf{r} is identical in magnitude to the change in the local pressure from the pressure far away, Δp . The perturbation in the total driving force can then be expressed in the form $\Delta A = A' \Delta p$ with

$$A' = \partial_p \left(\frac{\check{p}}{T} (\mu_l - \mu_s) \right) \Big|_T + \frac{1}{T}. \quad (64)$$

Using the properties of aluminum, one finds that the non-local contribution, i.e., the second term on the right-hand side of Eq. (64), is approximately 13.1 times larger than the homogeneous contribution, in the entire range $T = [900, 960]$ and $p = [0.8p_0, 1.2p_0]$. On the other hand, if a similar analysis is performed for a temperature perturbation at constant homogeneous pressure, the inhomogeneous contribution to the total change in the driving force is approximately a factor 10^{-4} smaller than the homogeneous contribution. Therefore, we conclude that for practical purposes the inhomogeneities in the temperature can be neglected in $A_{\text{non-iso}}$, in contrast to the inhomogeneities in the pressure, which are essential and may even overrule the effects of the homogeneous term.

The effect of the non-local term on the driving force can also be expressed in terms of a change in melting temperature, which is defined through $A = 0$. To illustrate this, we consider the following scenario. On the one hand, we take a homogeneous situation described by (T, p) . Applying a homogeneous change in the pressure, Δp , results in a change of the melting temperature, $\Delta T_{m, \text{hom}}$. This we compare with another case where locally at position \mathbf{r} the temperature and pressure are identical to the homogeneous case, namely (T, p) , but

the non-local term has a contribution of the size $\Delta p/T$, with the same value for Δp as in the homogeneous case. Then there is also a change in the melting temperature, denoted by $\Delta T_{m,\text{non-loc}}$. For aluminum, one finds that

$$\frac{\Delta T_{m,\text{non-loc}}}{\Delta T_{m,\text{hom}}} \simeq 13.1, \quad (65)$$

i.e., the change in melting temperature due to a curvature in the pressure profile is considerably larger than for an equivalent change in the bulk pressure. We mention that comparing a shift in the bulk pressure, Δp , to the effect of the inhomogeneous contribution to the crystallization, $\lambda_2 \nabla \cdot \nabla p$, is only a condition on the combination of λ_2 together with the curvature in the pressure profile, but at this stage it is not resolved whether a large value in $\lambda_2 \nabla \cdot \nabla p$ is primarily due to a long screening length, $\sqrt{|\lambda_2|}$, or due to a high curvature. The effect of λ_2 is discussed below.

4.3. Perturbation analysis

The dynamic model given in Eqs. (39)–(42) is complicated to simulate for two reasons. First, it contains fourth-order spatial derivatives of the temperature and of the pressure, which makes the specification of reasonable boundary conditions particularly difficult (see also [31]). Fourth-order derivatives also occur in the theory of the deformation of beams and plates [32], in the Kuramoto–Sivashinsky equation [33, 34], and in the Cahn–Hilliard equation [35, 36]. Most simulations, in particular of the latter, assume periodic boundary conditions. The second complication concerns the difference in mass densities of the solid and liquid phases, due to which the domain changes in time as crystallization proceeds. This precludes the application of periodic boundary conditions under general circumstances.

However, the complications due to the domain change can be avoided in the one-dimensional case if the situation is symmetric with respect to $z = 0$ or if one end of the domain is bound by a fixed wall at $z = 0$. In order to simplify the equations, one can then make a transformation of variables from z to

$$\bar{z}(z, t) := \int_0^z \rho(z', t) dz'. \quad (66)$$

This transformation of variables is analogous to the one employed in the simulation of multicomponent diffusion in liquids [37, 38]. If the time-dependent maximal extension of the domain is denoted by $z_{\text{max}}(t)$, the upper limit $\bar{z}(z_{\text{max}}(t), t) = \mathcal{M}_0$ is independent of time, because it simply represents the total mass (per constant cross-sectional area) contained in the range

$[0, z_{\max}(t)]$. Furthermore, one can show by virtue of the balance equation for the total mass (see Eqs. (32) and (33)), that the derivative operators in Eqs. (40)–(43) transform as follows:

$$\left. \frac{\partial}{\partial t} \right|_z + (v + v_{\text{pc}}) \left. \frac{\partial}{\partial z} \right|_t = \left. \frac{\partial}{\partial t} \right|_{\bar{z}}, \quad (67)$$

$$\left. \frac{\partial}{\partial z} \right|_t = \rho \left. \frac{\partial}{\partial \bar{z}} \right|_t, \quad (68)$$

where we have assumed that $(v + v_{\text{pc}})(0, t)\rho(0, t) = 0$. In particular, we note that the material derivative in the original equations reduces to the partial derivative $(\partial \cdot / \partial t)|_{\bar{z}}$ at constant \bar{z} , in contrast to when z is kept constant. Using the transformation (66), the domain is constant, and we can easily impose periodic boundary conditions at the ends of this stationary domain.

In order to analyze the effect of the parameter λ_2 , we perform a perturbation analysis around a stationary state of Eqs. (40)–(43) on the melting line, namely around

$$v_0 = 0, \quad (69)$$

$$T_0 = T_m, \quad (70)$$

$$p_0 = p_m, \quad (71)$$

$$\phi_0 = 1/2. \quad (72)$$

The analysis of the relaxation in space and time of the perturbation is simplified drastically by the ansatz

$$\Delta v(\bar{z}, t) = \Delta v_1(t) + \Delta v_2(t) \cos(2\pi\bar{z}/M_0), \quad (73)$$

$$\Delta T(\bar{z}, t) = \Delta T_1(t) + \Delta T_2(t) \sin(2\pi\bar{z}/M_0), \quad (74)$$

$$\Delta p(\bar{z}, t) = \Delta p_1(t) + \Delta p_2(t) \sin(2\pi\bar{z}/M_0), \quad (75)$$

$$\Delta \phi(\bar{z}, t) = \Delta \phi_1(t) + \Delta \phi_2(t) \sin(2\pi\bar{z}/M_0), \quad (76)$$

with $M_0 = \rho(T_0, p_0, \phi_0)L_0$ and L_0 the periodicity of the simulation unit or, conversely, the wavelength of the perturbation. In this case, each derivative with respect to \bar{z} is replaced by a factor $2\pi/M_0$, and it can be shown that the explicit space-dependence drops out in all equations. The perturbation analysis thus reduces to studying the eigenvalues of a relaxation matrix in time.

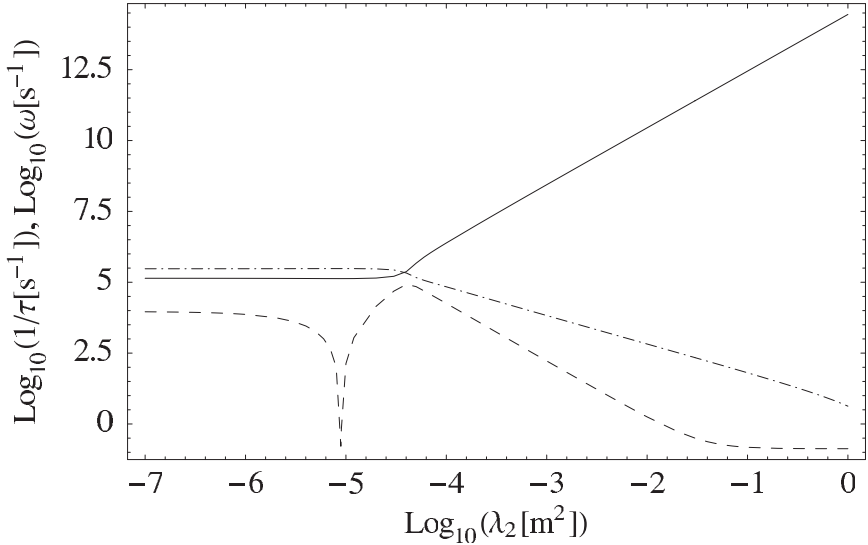


Figure 1 Eigenvalues of the relaxation matrix as a function of the parameter λ_2 for a perturbation on the length scale $L_0 = 0.1$ m. One eigenvalue is real corresponding to a single exponential (solid line), while the other two eigenvalues represent exponentially damped oscillations with frequency ω (dashed-dotted line) and relaxation time τ of the envelope (dashed line).

The relaxation matrix for the homogeneous perturbation $(\Delta v_1, \Delta T_1, \Delta p_1, \Delta \phi_1)$ has three zero eigenvalues and one single exponential decay with decay rate $\tau \simeq 6.37 \mu\text{s}$. While the homogeneous perturbation is for obvious reasons insensitive to both, the box length L_0 and the parameter λ_2 , the situation is more complicated for the heterogeneous perturbations, $(\Delta v_2, \Delta T_2, \Delta p_2, \Delta \phi_2)$. The eigenvalues of the corresponding relaxation matrix are either real, corresponding to single exponential decay, or they come in pairs of the form $(1/\tau + i\omega, 1/\tau - i\omega)$, representing exponentially damped oscillations of frequency ω . Figures 1 and 2 show the dependence of the eigenvalues on λ_2 , for $L_0 = 0.1$ m and $L_0 = 0.001$ m, respectively. In both cases, one of the four eigenvalues is equal to zero and is therefore not discussed any further in the following.

In Figure 1 for $L_0 = 0.1$ m, one eigenmode is decaying exponentially, while the two other eigenmodes are damped oscillations with decay time τ and frequency ω . Note that the graph covers a wide range for the scanning length $\sqrt{\lambda_2}$, namely from $\sqrt{\lambda_2} \simeq 3.2 \times 10^{-3} L_0$ to $\sqrt{\lambda_2} = 10 L_0$, i.e., it ranges from much shorter to longer than the wavelength of the perturbation. The limiting values $\lambda_2 \rightarrow 0$ in the graph correspond to the results obtained for $\lambda_2 = 0$.

Although Figure 2 for $L_0 = 0.001$ m covers a similar relative range as in Figure 1, namely from $\sqrt{\lambda_2} \simeq 3.2 \times 10^{-3} L_0$ to $\sqrt{\lambda_2} = 100 L_0$, the situation is

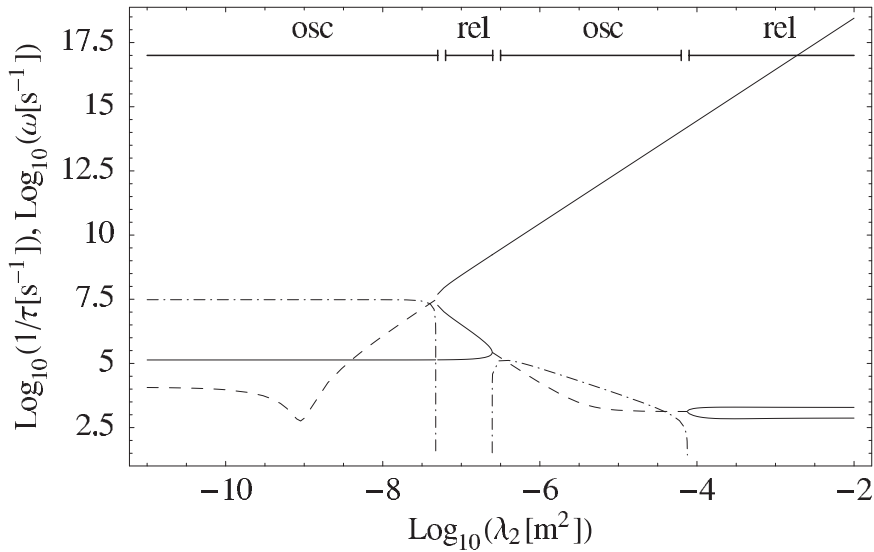


Figure 2 Eigenvalues of the relaxation matrix as a function of the parameter λ_2 for a perturbation on the length scale $L_0 = 0.001$ m. In the regions of λ_2 denoted by “rel”, all three eigenvalues correspond to single exponential relaxation. In the regions named “osc”, only one eigenvalue represents single exponential decay (solid line), while the other two eigenvalues represent exponentially damped oscillations with frequency ω (dashed-dotted line) and relaxation time τ of the envelope (dashed line).

more complicated. In certain regions of λ_2 denoted by “rel” in Figure 2, all three eigenvalues are real, i.e., any perturbation decays exponentially. In other regions, denoted by “osc” in Figure 2, one has the same situation as for $L_0 = 0.1$ m, i.e., one eigenvector decays exponentially while the other two decay by a damped oscillation with frequency ω and decay time τ of the envelope. Figure 2 also nicely shows that at the edges of the oscillatory to the purely exponential regions, one finds $\omega \ll 1/\tau$, which illustrates the transition from a damped oscillation via an overdamped oscillation to purely exponential relaxation.

The common feature to Figures 1 and 2 is that if $\sqrt{\lambda_2}$ is comparable to the characteristic length scale of the perturbation, L_0 , an exponential decay becomes very fast while the other two modes become slow, be it exponential decay or damped oscillation. This can be explained as follows. In this range of $\sqrt{\lambda_2}$ values, the non-isochore contribution to the driving force smooths out the influence of the inhomogeneities in the pressure and temperature on the driving force. In this sense, the equilibration of pressure through the corresponding inhomogeneous rate of phase transformation is slowed down for increasing $\sqrt{\lambda_2}$. On the other hand, increasing value of $\sqrt{\lambda_2}$ results in a larger phase change contribution to the transport velocity, which is expressed through a time scale becoming faster.

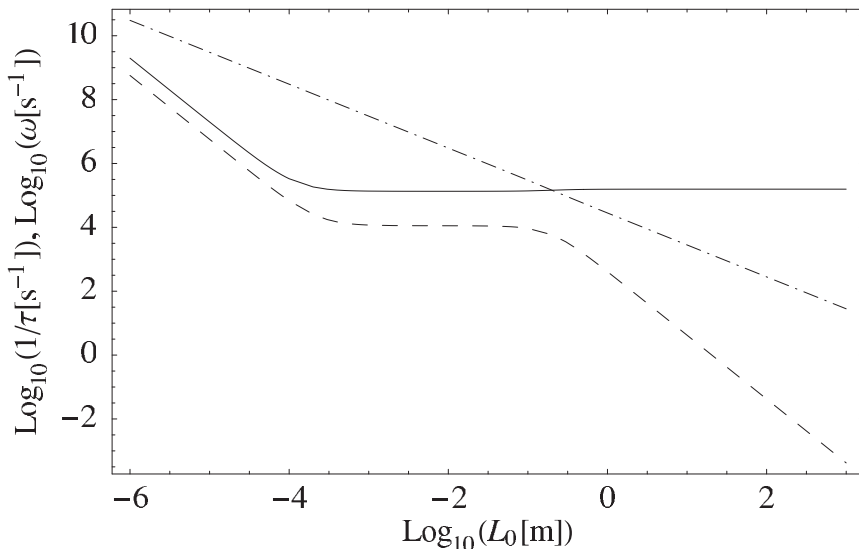


Figure 3 Eigenvalues of the relaxation matrix as a function of the length scale of the perturbation, L_0 , for $\lambda_2 = 0$. One eigenvalue is real corresponding to a single exponential (solid line), while the other two eigenvalues represent exponentially damped oscillations with frequency ω (dashed-dotted line) and relaxation time τ of the envelope (dashed line). One finds $\omega \propto L_0^{-1}$, and the relaxation time scales as $\tau \propto L_0^2$ at low and high values of L_0 .

While Figure 1 showed only quantitative variations as a function of the parameter λ_2 , Figure 2 shows qualitative variations. If one assumes that the value of λ_2 is known, the data in Figures 1 and 2 suggests that for a general perturbation the various wavelengths not only decay at different rates, but some of them decay in an oscillatory manner and others purely exponentially. This is a feature specific to $\lambda_2 \neq 0$ because for $\lambda_2 = 0$ the character of the spectrum of eigenvalues does not change as a function of the wavelength of the perturbation, L_0 , as shown in Figure 3 for a considerable range of perturbation wavelengths.

5. Discussion

A simplified crystallization model has been developed in terms of the average momentum density, a single temperature, a single pressure, and the volume fraction of the crystalline phase. The unnecessary but commonly employed restriction that the phase transformation occurs instantaneously at constant volume has been relaxed in the treatment presented here. Namely, we allow for a dissipative mass current that is proportional to the rate of crystallization/melting. Rather than introducing an additional variable, this dissipative current is expressed in terms of the temperature, pressure and volume fraction

through a constitutive relation. Including this dissipative current in the description, we found that by way of the Onsager–Casimir symmetry the driving force for phase change is modified. In particular, it does not only depend on the local chemical potential difference, but it also contains a non-local term, namely the Laplacian of the ratio p/T multiplied by the square of a screening length.

The consequences of including the dissipative current and the non-local contribution to the driving force have been discussed in detail, and for the specific case of aluminum a perturbation analysis has been performed. The results have shown the strong dependence of the eigenvalues of the relaxation matrix on the value of the screening length. It is worth mentioning that in Figures 1 and 2 the oscillations become less virulent (i.e., lower value of ω) the higher the screening length parameter, λ_2 . This can be traced back to the expression for the full driving force, A in Eq. (27), by which potential phase transformations are slowed down if they are unfavorable with respect to the pressure conditions in the vicinity. Therefore, less dramatic pressure variations are building up, and hence the pressure equilibration is smoother for increasing screening length. So, there are two fundamentally different ways in which one can view the inclusion of the dissipative current \mathbf{j}_{pc} and the non-local contribution $A_{\text{non-iso}}$. On the one hand, it is the implementation of the ideas presented in the Introduction, and relaxing the restriction of phase transformation being instantaneously isochore. On the other hand, one can view the model with included dissipative current as a slow, i.e., smoothed, version of the case $\lambda_2 = 0$, because the parameter λ_2 helps to avoid large pressure changes. Along the lines of this latter view, one can argue that, e.g., in melting conditions with the solid being more dense than the liquid, a drastic pressure increase due to melting in the case $\lambda_2 = 0$ would be counteracted or even reversed because of the influence of the pressure on the driving force. Therefore, the non-local term in the driving force has a tendency to avoid or at least smooth out such situations.

Finally, we draw the connection to single-phase hydrodynamics, in particular, when formulated in terms of the variables $\{\mathbf{u}, T, p\}$. In the two-phase model above, the distinction between conditions that arise from the non-equilibrium thermodynamics technique, and additional conditions that were imposed by physical intuition has been pointed out in several instances. In particular, the functions Ω_\star , $\bar{\Omega}_\star$, and $\Omega_\star^{\eta, \lambda_{\text{th}}}$ ($\star = T, p, \phi$) only turned out to be given by Eqs. (44)–(52) because the rigorous conditions (16), (17), (23), (26), (80), (81) were supplemented by the additional constraints (18), (31) with $\bar{\rho}_s = \rho_s$, and (82). At least for the two additional constraints (18) and (82) we can offer further motivation. If the non-isothermal hydrodynamics equations for a single-phase fluid are written in terms of the variables $\{\mathbf{u}, T, p\}$, one obtains the equations (39)–(41) with $\mathbf{v}_{pc} = \mathbf{0}$ and

$\bar{\Omega}_T = \bar{\Omega}_p = \check{T} = \check{p} = 0$. The functions Ω_T , Ω_p , $\Omega_T^{\eta, \lambda_{\text{th}}}$, $\Omega_p^{\eta, \lambda_{\text{th}}}$ are identical to the two-phase expressions in Eqs. (44), (45), (50), (51) after replacing the average values by the single-phase properties of the material. In particular, we emphasize that this result is obtained for the single-phase hydrodynamics without any additional constraints, i.e., the constraints imposed by the thermodynamics formalism are sufficient to determine these functions uniquely. Therefore, this finding supports a posteriori the additional constraints (18), (82) in the two-phase model.

Acknowledgements

The author thanks Profs. Hans Christian Öttinger, Daniel Lhuillier, and Manuel Laso, and Drs. André Bardow and Ilya Karlin for stimulating discussions. The help of Prof. Peter J. Uggowitzer and Drs. Bengt Hallstedt, Thomas Schweizer, and Alain Jacot with finding the experimental data for aluminum is gratefully acknowledged.

Appendix: Viscous stresses, thermal conduction

In order to determine the GENERIC dissipative matrix \mathbf{M} associated to heat conduction and viscous stress, we point out that these two effects do not specifically address the difference between a one- and a two-phase system. We may thus start from the dissipative matrix for a single-phase system, which has been treated in terms of the variables $\{\rho, \mathbf{u}, e\}$ (see p. 58 in [11]). The corresponding matrix elements are abbreviated here as $M_{\mathbf{uu}}$, $M_{\mathbf{ue}}$, $M_{e\mathbf{u}}$, and M_{ee} , while all other five elements are zero, because the mass density balance is not affected by these effects. Correspondingly, in the two-phase model presented here, the individual mass balance equations for the solid and liquid phases should also not be affected by the viscous stress or the thermal conduction. For the matrix representing viscous flow and thermal conduction, we thus propose the form

$$\mathbf{M}^{\eta, \lambda} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & \Omega_T^{\eta, \lambda_{\text{th}}} \\ 0 & \Omega_p^{\eta, \lambda_{\text{th}}} \\ 0 & \Omega_\phi^{\eta, \lambda_{\text{th}}} \end{pmatrix} \cdot \begin{pmatrix} M_{\mathbf{uu}} & M_{\mathbf{ue}} \\ M_{e\mathbf{u}} & M_{ee} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{1} & 0 & 0 & 0 \\ 0 & \Omega_T^{\eta, \lambda_{\text{th}}} & \Omega_p^{\eta, \lambda_{\text{th}}} & \Omega_\phi^{\eta, \lambda_{\text{th}}} \end{pmatrix}, \quad (77)$$

where the functions $(\Omega_T^{\eta, \lambda_{\text{th}}}, \Omega_p^{\eta, \lambda_{\text{th}}}, \Omega_\phi^{\eta, \lambda_{\text{th}}})$ take care of the mapping from the variables (T, p, ϕ) on the mass density ρ . The formulation of the matrix elements $M_{\mathbf{uu}}$, $M_{\mathbf{ue}}$, $M_{e\mathbf{u}}$, and M_{ee} for a single-phase fluid is based on having

$\delta E/\delta \mathbf{u} = \mathbf{v}$, $\delta E/\delta e = 1$, $\delta S/\delta \mathbf{u} = \mathbf{0}$, and $\delta S/\delta e = 1/T$, and therefore in the formulation with $\mathbf{x} = (\mathbf{u}, T, p, \phi)$ this is expressed as

$$\begin{pmatrix} \mathbf{1} & 0 & 0 & 0 \\ 0 & \Omega_T^{\eta, \lambda_{\text{th}}} & \Omega_p^{\eta, \lambda_{\text{th}}} & \Omega_\phi^{\eta, \lambda_{\text{th}}} \end{pmatrix} \cdot \frac{\delta E}{\delta \mathbf{x}} = \begin{pmatrix} \mathbf{v} \\ 1 \end{pmatrix}, \quad (78)$$

$$\begin{pmatrix} \mathbf{1} & 0 & 0 & 0 \\ 0 & \Omega_T^{\eta, \lambda_{\text{th}}} & \Omega_p^{\eta, \lambda_{\text{th}}} & \Omega_\phi^{\eta, \lambda_{\text{th}}} \end{pmatrix} \cdot \frac{\delta S}{\delta \mathbf{x}} = \begin{pmatrix} \mathbf{0} \\ \frac{1}{T} \end{pmatrix}. \quad (79)$$

The degeneracy condition (5) in the form of Eq. (78) and the conservation of total mass lead to the constraints

$$\Omega_T^{\eta, \lambda_{\text{th}}} e_{,T} + \Omega_p^{\eta, \lambda_{\text{th}}} e_{,p} + \Omega_\phi^{\eta, \lambda_{\text{th}}} e_{,\phi} = 1, \quad (80)$$

$$\Omega_T^{\eta, \lambda_{\text{th}}} \rho_{,T} + \Omega_p^{\eta, \lambda_{\text{th}}} \rho_{,p} + \Omega_\phi^{\eta, \lambda_{\text{th}}} \rho_{,\phi} = 0. \quad (81)$$

It can be shown that in order to comply also with Eq. (79), one needs the condition

$$\Omega_T^{\eta, \lambda_{\text{th}}} \rho_{s,T} + \Omega_p^{\eta, \lambda_{\text{th}}} \rho_{s,p} + \Omega_\phi^{\eta, \lambda_{\text{th}}} \rho_{s,\phi} = 0, \quad (82)$$

which determines the three functions $(\Omega_T^{\eta, \lambda_{\text{th}}}, \Omega_p^{\eta, \lambda_{\text{th}}}, \Omega_\phi^{\eta, \lambda_{\text{th}}})$ uniquely.

The dissipative matrix (77) together with the conditions (80)–(82) inherits the symmetry, positive semi-definiteness, and the degeneracy (5) from the single-phase matrix. Application of the two right-most matrices in Eq. (77) to $\delta S/\delta \mathbf{x}$ results in the usual dissipative contributions to the equations for the momentum density and the internal energy density, respectively (see [11] for details), with Newton's expression for the viscous pressure tensor and Fourier's law of heat conduction,

$$\boldsymbol{\tau} = -\eta \dot{\boldsymbol{\gamma}} - \left(\frac{\kappa_v}{2} - \frac{\eta}{3} \right) (\text{tr } \dot{\boldsymbol{\gamma}}) \mathbf{1}, \quad (83)$$

$$\mathbf{j}_q = -\lambda_{\text{th}} \cdot \nabla T, \quad (84)$$

with viscosity η and bulk viscosity κ_v , the symmetrized velocity gradient tensor $\dot{\gamma}_{ij} = \partial_i v_j + \partial_j v_i$, and the thermal conductivity tensor λ_{th} . Subsequent multiplication with the left-most matrix on the right-hand side of Eq. (77) maps these dissipative contributions properly from the momentum density and energy density onto the variables $\mathbf{x} = (\mathbf{u}, T, p, \phi)$.

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Paper received: 2005-07-04

Paper accepted: 2005-09-01

