

Dynamic mean-field models from a nonequilibrium thermodynamics perspective

Citation for published version (APA):

Hütter, M., Karlin, I. V., & Öttinger, H. C. (2003). Dynamic mean-field models from a nonequilibrium thermodynamics perspective. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 68(1), 016115-1/9. Article 016115. <https://doi.org/10.1103/PhysRevE.68.016115>

DOI:

[10.1103/PhysRevE.68.016115](https://doi.org/10.1103/PhysRevE.68.016115)

Document status and date:

Published: 01/01/2003

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Crystallization under external pressure

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Received 3 September 2003; received in revised form 22 October 2003

This article is part of a Special Volume containing papers from the 3rd International Workshop on Nonequilibrium Thermodynamics and Complex Fluids

Abstract

The influence of external pressure on the dynamics of crystallization is examined by considering a solid–liquid two-phase system in a cylinder closed by a piston. The dynamic equations are derived using three methods, namely, Rational Thermodynamics (Liu’s procedure), the Matrix Model, and the general equation for the nonequilibrium reversible–irreversible coupling (GENERIC) formalism. The constitutive relation for the multiphase pressure on the piston is identical for all three methods, whereas some aspects of the result for the phase change dynamics differ. The rational thermodynamics treatment constrains the phase change dynamics of only those structural variables that enter into the dissipation inequality, whereas the other two formalisms make statements about the phase change of all structural variables. Nevertheless, all three methods show, first, that the phase change happens instantaneously at constant volume and, second, where morphological detail can be built into the model without violating thermodynamic principles. It is discussed how an appropriate choice of the morphological variables allows one to incorporate impingement of crystals and depletion zone effects, as well as to distinguish crystal shapes.

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Keywords: Phase change; Nonequilibrium thermodynamics; Morphology

1. Introduction

The reasons for liquid–solid phase transitions are many. Apart from cooling, external pressures influence the transition as well, which we concentrate on in this paper. Let us consider two prominent examples of how external pressure influences crystallization and melting, respectively. First, carbon solidifies into graphite at pressures below $p \approx 10^{10}$ Pa upon cooling, whereas above this pressure it forms diamond, the latter being only metastable at ambient conditions. Another example of the pressure influence can be found by studying the phase diagram of H₂O: at atmospheric pressure, the water–ice coexistence line has a negative slope, i.e. $dp/dT < 0$. By means of the Clausius–Clapeyron relation this translates into the ice being less dense than water, therefore ice can be melted by applying pressure, contrary to most other materials. However, at pressures above $p \approx 10^9$ Pa, ice is more dense than water and the coexistence line has a positive slope.

Whereas equilibrium thermodynamics offers means to determine the stable phase and to discuss the phase diagram, it does not describe the dynamics of the phase transition. The latter can be described by nonequilibrium thermodynamics approaches, which determine the thermodynamic contributions to the driving force for the phase change, but do not restrict the form of the kinetic effects, i.e. of the time scales, as will be shown below. In this paper, the influence of external pressure on the dynamics of crystallization is examined by considering a solid–liquid two-phase system similar to [1], here in a cylinder closed by a piston. Dynamic equations are derived using three different methods, namely, Rational Thermodynamics (Liu’s procedure) [2–4], the Matrix Model [5–7], and the general equation for the nonequilibrium reversible–irreversible coupling (GENERIC) formalism [8,9]. The GENERIC formalism has been compared with the Matrix Model [10] and with the rational nonequilibrium thermodynamics method [11] for the example of a single-phase system enclosed in a piston without phase change. We here extend these comparisons by including a phase change with a detailed description of the morphology.

The manuscript is organized as follows. First, the level of description used in this study is introduced and motivated in Section 2, and the points of special interest are high-

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lighted. After discussing the three thermodynamic methods in Section 3, they are applied to study crystallization under external pressure, and their results are compared in Section 4. Finally, the main conclusions are drawn and discussed in Section 5.

2. Description of the system

2.1. Choice of variables

The choice of variables to describe a system which exhibits a solid–liquid phase transition depends on the physics one aims at describing. In this study, the focus is on the effect of an external pressure. Therefore, a description of the two phases on the level of their thermodynamic states, i.e. pressures, chemical potentials, and temperatures, is appropriate to capture the main effects of an externally applied pressure. In other words, we study the coupling of external conditions to internal variables which are on the same level of coarse-graining.

The thermodynamic states of the individual phases can be described by the total mass of liquid and solid, M_l and M_s , and the total volumes, V_l and V_s . Furthermore, we intend to study the system on time scales on which the two-phases equilibrate the temperature and on which all kinetic energy of the small crystallites and of the liquid phase is already transferred into internal energy. Thus, to account for thermal effects, one can either choose the system temperature T as a further variable or the total internal energy U .

The choice of variables to capture the morphology is strongly inspired by integral geometry. There, closed surfaces in three-dimensional space are most naturally described in terms of four so-called Minkowski functionals (also quermass integrals, curvature integrals). For more details, the reader is referred to [12–16]. For a given surface, these functionals include the volume (length^3), the total surface of the interface (length^2), the surface integral of the mean curvature (length^1), and the connectivity (number of components plus cavities, minus number of tunnels) (length^0), the latter measuring the topology. In the solid–liquid two-phase system under consideration here, it is intuitive to consider the solid phase as composed of overlapping, impinging grains (see also Fig. 1). In the case of overlap, the Minkowski functionals for the union of grains differ from the sums of the single grain Minkowski functionals. We here choose to use the volume, V_s , and surface, A , of the union of overlapping grains, i.e. of the real structure, whereas the sum of the individual grain mean curvature integral and the number of grains, denoted by L and N , are used for the following reasons. When expressing bulk and surface contributions to thermodynamic potentials, clearly the properties of the union of overlapping grains rather than of the single grains are physically relevant. However, for calculating a configurational entropy for the arrangement of the grains in space, the number of grains is preferable

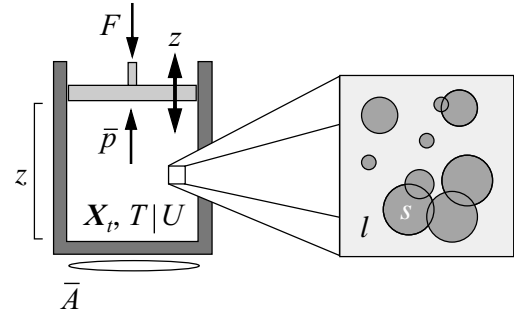


Fig. 1. Solid (s)–liquid (l) two-phase system in a cylinder closed by a frictionless piston. Symbols as introduced in the text.

to the complicated topological measure connectivity. As for the characteristic length scale, we choose the mean curvature integral as summed over the individual grains, rather than as determined for the union of grains. This choice of variables has also been applied in a previous study [1]. We note that it is essential to include not only the volume of the crystalline phase, V_s , but all four morphological variables. The reason is that this allows us to include surface tension effects, impingement of crystallites, depletion zone effects, and to distinguish crystal shapes, as will become clear below.

Last but not least, the linear momentum of the piston (of mass m) is denoted by P , whereas the piston position z can be expressed in terms of the variables chosen above,

$$z = \frac{1}{\bar{A}}(V_l + V_s), \quad (1)$$

\bar{A} being the cross-section of the piston. In conclusion, the variables to describe the system are

$$\mathbf{x} = (P, x_{\text{th}}) \oplus \mathbf{X}_t, \quad (2)$$

with the thermal variable x_{th} either $x_{\text{th}} = T$ or $x_{\text{th}} = U$, and

$$\mathbf{X}_t = (M_l, M_s, V_l, V_s, A, L, N) \quad (3)$$

Note that we have assumed that the interface is massless. The current set of variables allows one to capture a temperature dependent surface tension, if the variables A and x_{th} are supplemented with the appropriate thermodynamic potential for the interface. Fig. 1 summarizes the setup of the system as well as the meaning of the variables.

2.2. Dynamic equations: terms of special interest

The formulation of a dynamic model for crystallization in terms of the variables (2) is a formidable task and it is useful to use thermodynamic methods to do so. However, one can formulate part of the model without thermodynamic methods, and use the latter to determine certain constitutive relations. In the following, we formulate the overall structure of the dynamic equations for the variables (2), and point out which particular ingredients therein need thermodynamic methods for their discussion.

The piston momentum changes only due to potential forces, $-\partial_z V(z)$, external pressures p_{ext} , and internal pressure due to the two-phase system enclosed in the cylinder, \bar{p} , if we assume frictionless motion. As the piston moves and changes the total volume in the cylinder, $d/dt(V_1 + V_s) = \bar{A}P/m$, also the individual phases change their volumes. In the case of different compressibilities, the phases change volume in a complex manner, as is also the case for the other morphological variables A , L . The number of crystals, N , is not affected by a change in volume. In the dynamic equations for these properties, these compressibility effects due to change in piston momentum can be captured by terms explicitly proportional to the rate $\bar{A}P/m$ with rate independent prefactors. As far as the phase change contributions are concerned, one notes that the phase change contributions to the two mass balances must add up to zero due to mass conservation, and that the mass transfer is connected to the volume transfer by means of a mass density, denoted as $\hat{\rho}$ below. In summary, one finds

$$\dot{P} = -\partial_z V(z) + \bar{A}(\bar{p} - p_{\text{ext}}), \quad (4a)$$

$$\dot{M}_1 = -\hat{\rho}\Upsilon_V, \quad (4b)$$

$$\dot{M}_s = +\hat{\rho}\Upsilon_V, \quad (4c)$$

$$\dot{V}_1 = (1 - \kappa_V + \varepsilon_1)(\bar{A}P/m) - (1 + \varepsilon_2)\Upsilon_V, \quad (4d)$$

$$\dot{V}_s = \kappa_V(\bar{A}P/m) + \Upsilon_V, \quad (4e)$$

$$\dot{A} = \kappa_A(\bar{A}P/m) + \Upsilon_A, \quad (4f)$$

$$\dot{L} = \kappa_L(\bar{A}P/m) + \Upsilon_L, \quad (4g)$$

$$\dot{N} = \Upsilon_N, \quad (4h)$$

where the yet unspecified functions Υ_μ ($\mu = V, A, L, N$) are introduced through (4e–4h) to denote the phase change contributions of the specific variable.

The parameters ($\varepsilon_1, \varepsilon_2$) are introduced into Eq. (4d) for later use in order to discuss the splitting of reversible and irreversible contributions as required for the Matrix Model and the GENERIC formalisms, but not for the rational thermodynamics treatment. As we neglect friction of the piston, the phase change terms, proportional to Υ_μ ($\mu = V, A, L, N$) in the above Eq. (4), are the only irreversible terms, whereas all others are reversible in nature. While κ_V relates the change in total volume to the change in solid volume per definition, is it not apriori known if the corresponding coefficient for the liquid phase compression is simply $1 - \kappa_V$. Thus, we introduced the parameter ε_1 to account for such a possibility. The parameter ε_2 is introduced for analogous reasons to measure the phase change contribution for the liquid phase in terms of Υ_V , while Υ_V is defined as the phase change of the solid phase.

The equation for the thermal variable $x_{\text{th}} = T$ or $x_{\text{th}} = U$, respectively, has not been specified because that depends on whether one considers an isothermal or an adiabatic system, and is different for the various thermodynamics formalisms

used. The corresponding evolution equations will be discussed below.

A practically applicable model can be obtained from the above dynamic Eqs. (4) after, first, specifying the potential $V(z)$ and the external pressure p_{ext} , second, determining the parameters ε_1 and ε_2 , and third, choosing constitutive relations in terms of the variables \mathbf{x} (2) for the pressure on the piston \bar{p} , for the “compressibilities” κ_μ ($\mu = V, A, L$), and for the phase change contributions Υ_μ ($\mu = V, A, L, N$). These parameters and constitutive relations shall be examined using thermodynamic methods in Section 4, after introducing the methods in the following section.

3. Nonequilibrium thermodynamics methods

A specific system of interest can be described by several thermodynamic approaches. Since they all aim at describing the same physical systems, there must be interrelations between them, although they differ in the degree of detail with regard to the mechanics and thermodynamics of the description. We here choose to compare three methods, namely, Liu’s procedure of rational nonequilibrium thermodynamics, the Matrix Model, and the GENERIC formalism. They are briefly introduced in this section, before applying and comparing them in the following section on the specific example of the crystallization in a cylinder.

3.1. Rational nonequilibrium thermodynamics; Liu’s procedure

Here, we briefly describe the procedure of Liu of rational nonequilibrium thermodynamics. For more details the reader is referred to [2–4]. In order to introduce Liu’s procedure we consider a set of global balance equations for functions $\mathbf{a} = \mathbf{a}(\mathbf{x})$ of the variables \mathbf{x} ,

$$\dot{\mathbf{a}} = \boldsymbol{\Sigma}, \quad (5)$$

appropriate for this study. We emphasize however that the method can be used also for systems of local balance equations. Substituting the constitutive equations $\mathbf{a}(\mathbf{x})$ and $\boldsymbol{\Sigma}(\mathbf{x})$ into Eq. (5) and using the chain rule of differential calculus, we obtain from the above balance equations the balances on state space [3], which are linear in the higher derivatives of the variables, $\dot{\mathbf{x}}$. With $\mathbf{y} \equiv \dot{\mathbf{x}}$, the balance equations and the dissipation inequality can be represented by the matrix equations [4]

$$\mathbf{A} \cdot \mathbf{y} = \mathbf{C}, \quad (6a)$$

$$\mathbf{B} \cdot \mathbf{y} \geq D \quad (6b)$$

The domain of the matrices $\mathbf{A}(\mathbf{x})$, $\mathbf{C}(\mathbf{x})$, $\mathbf{B}(\mathbf{x})$ and $D(\mathbf{x})$ is given by the set of variables \mathbf{x} and does not include their higher derivatives \mathbf{y} , whereas their range is the entire state space. The dissipation inequality can be exploited by using Liu’s lemma:

Proposition. *If all solutions y of the balance equations $A \cdot y = C$ satisfy the dissipation inequality $B \cdot y \geq D$, state-space functions $\Lambda(x)$ exist for which the Liu equations and the reduced dissipation inequality are valid:*

$$A \cdot A = B, \quad (7a)$$

$$A \cdot C \geq D \quad (7b)$$

The special presupposition of this proposition that *all* solutions of the balance equations satisfy the dissipation inequality is called the Coleman–Mizel formulation of the second law [17], which can be proven by an amendment of the second law [3].

3.2. Matrix Model

The Matrix Model [5–7] is different from the other two thermodynamic formalisms presented here in that it makes a clear distinction between a thermodynamic subsystem and its environment. The environment is described by controllable external forces F_e and rates \dot{x}_e , in contrast to the internal variables x and the thermodynamic conjugate forces F_x of the subsystem. For example, in the adiabatic case one has $F_x = (\partial U / \partial x)_S$ and in the isothermal case $F_x = (\partial F / \partial x)_T$, with internal energy U , entropy S , Helmholtz free energy F , and absolute temperature T . The dissipation rate, Δ , is then obtained as the difference between the rate of power supplied to the subsystem and the internal rate of change of energy,

$$\Delta = F_e \odot \dot{x}_e - F_x \circ \dot{x}, \quad (8)$$

where \odot and \circ denote the appropriate inner products. Based on the assumption that the state variables x and the dissipation Δ remain unchanged under a reversal of the sign of the external rates \dot{x}_e , the Matrix Model is derived:

$$\begin{pmatrix} F_e \\ \dot{x} \end{pmatrix} = \begin{pmatrix} \eta \odot & -\Lambda^T \circ \\ \Lambda \odot & \beta \circ \end{pmatrix} \begin{pmatrix} \dot{x}_e \\ -F_x \end{pmatrix}, \quad (9)$$

where all matrix elements may be functions of the externally controlled rate \dot{x}_e and the internal thermodynamic forces F_x and are even with respect to time reversal of the external rates \dot{x}_e . The operators η and β must both be symmetric and positive semi-definite. The operator Λ^T denotes the adjoint of Λ .

In contrast to the rational non-equilibrium thermodynamics treatment using Liu's procedure, the Matrix Model distinguishes conservative (i.e. reversible) from dissipative (i.e. irreversible) dynamics. By using the Matrix Model equations, one finds that the antisymmetric contributions in the matrix, i.e. Λ , do not contribute to the dissipation rate (8), whereas the symmetric part (η, β) does.

3.3. GENERIC formalism

Recently, a general equation for the nonequilibrium reversible-irreversible coupling has been developed for describing nonequilibrium systems [8,9]. In contrast to the

Matrix Model, GENERIC deals with isolated systems, i.e. the total energy is conserved as well as entropy production is non-negative. The set of independent variables that describe the physics of interest to sufficient detail shall here be denoted by x , which may have discrete as well as continuous indices. The time evolution of these variables x is then written in the form

$$\frac{dx}{dt} = L(x) \cdot \frac{\delta E}{\delta x} + M(x) \cdot \frac{\delta S}{\delta x}, \quad (10)$$

where the two generators E and S are the total energy and entropy functionals in terms of the state variables x , L and 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 $\delta / \delta x$ typically implies functional rather than partial derivatives (for more details see [8,9]). The GENERIC structure also imposes certain conditions on the building blocks in (10). First, Eq. (10) is supplemented by the degeneracy requirements

$$L(x) \cdot \frac{\delta S}{\delta x} = 0, \quad (11a)$$

$$M(x) \cdot \frac{\delta E}{\delta x} = 0 \quad (11b)$$

The requirement that the (functional) derivative of the entropy lies in the null space of L represents the reversible nature of L . On the other hand, the requirement that the functional derivative of the energy lies in the null space of M manifests that the total energy is not altered by the M -contribution to the dynamics. In addition to these degeneracy requirements, L must be anti-symmetric and fulfill the Jacobi identity, whereas 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. (10) implies both the conservation of total energy as well as a nonnegative entropy production. The two contributions to the time evolution of x generated by the total energy E and the entropy S in (10) are called the reversible and irreversible contributions, respectively.

4. Derivation of the dynamic equations for phase change

The dynamic equations for the crystallization model are developed in this section using the three different thermodynamic methodologies. Rather than completing the formulation for each method separately, we structure this chapter along the open questions concerning the balance Eqs. (4) as described at the end of Section 2, namely, discussion of the parameters ($\varepsilon_1, \varepsilon_2$) and of the constitutive relations in terms of the variables x for the pressure on the piston \bar{p} , for the compressibilities κ_μ ($\mu = V, A, L$), and for the phase change contributions Υ_μ ($\mu = V, A, L, N$). For each of these points, the three thermodynamic methodologies shall

be developed and compared in parallel. Doing so, the differences in the procedures and reasons for specific results is highlighted.

4.1. Phase change at constant volume

We start with discussing the balance equations for the liquid and solid phases as given by (4d, 4e). Since the volume changes of the two phases must add up to the change in total volume as controlled by the momentum of the piston, $\bar{A}P/m$, one finds the following constraint for the two parameters ($\varepsilon_1, \varepsilon_2$):

$$\varepsilon_1 \bar{A}P/m = \varepsilon_2 \Upsilon_V \quad (12)$$

It was pointed out when describing the thermodynamic methods, that the rational nonequilibrium thermodynamics technique does not split dynamic contributions into reversible and irreversible parts, whereas both the Matrix Model as well as GENERIC do. Inserting the constraint (12) into the balance Eq. (4d) deletes the parameters ($\varepsilon_1, \varepsilon_2$) altogether from a rational thermodynamics viewpoint, which can also be achieved by the stronger constraint $\varepsilon_1 = \varepsilon_2 = 0$.

However, for the Matrix Model and GENERIC the argument is different as not only the sum of the contributions is relevant, but also how they can be split into reversible and irreversible parts. The balance Eq. (4d) is written in a suggestive form such that the ε_1 -term is reversible, in contrast to the irreversible ε_2 -term. On the one hand, considering the constraint (12), one finds that since Υ_V depends on a crystallization rate, the variable ε_1 like-wise depends on that rate constant. On the other hand, both in the Matrix Model and in GENERIC, the reversible dynamics is driven by the gradient of a thermodynamic potential, multiplied by an antisymmetric operator. It is important to note that neither of these potential functions depends on any rate constants, but rather only capture information about states in terms of state variables. Furthermore, the reversible antisymmetric operators do not depend on any rate constants as this would violate their reversible nature. One is therefore lead to the conclusion that the parameters must satisfy $\varepsilon_1 = 0$, and by virtue of (12) also $\varepsilon_2 = 0$.

In conclusion, all three thermodynamic methods find the same constraints,

$$\varepsilon_1 = \varepsilon_2 = 0, \quad (13)$$

although on different grounds. Physically, this result stands for the fact that compressing the two-phase system instantaneously affects the phases through compression effects only, or vice versa, that phase change happens at constant volume, at least instantaneously. It is an experimental fact that crystallization or melting between two phases of different mass densities will eventually move the piston. However, the result (13) tells us that phase transformation only indirectly moves the piston, by changing the pressures in the phases and thereby also altering the pressure \bar{p} (see Fig. 1) on the

piston. We therefore proceed to examine how the pressure \bar{p} relates to the pressures of the single phases.

4.2. Internal pressure on the piston

The determination of the constitutive relation for multi-phase pressure \bar{p} on the piston is the main goal of this section. This can only be done by carefully defining the set of independent variables and the appropriate thermodynamic potentials for each of the three thermodynamic methods examined here. As a reference for the further discussion, the reader is referred to the Table 1 for a short comparison of the methods' levels of description.

Using rational nonequilibrium thermodynamics to describe the system, one starts with identifying the building blocks in (6a, 6b) with the dynamic Eq. (4). Assuming that the cylinder is thermally insulated, i.e. that the heat flux through the cylinder walls and across the piston is always strictly zero, the dissipation inequality (6b) represents non-negative entropy production, $\dot{S} \geq 0$. Since the entropy is the potential of interest, the corresponding thermal variable is the internal energy, $x_{th} = U$. Thus, the entire system is described by

$$\mathbf{x}_{RTD} = (P, U) \oplus \mathbf{X}_t, \quad (14)$$

where \mathbf{X}_t is defined by (3). In the absence of heat fluxes through the cylinder surface, the total energy $E = P^2/2m + V(z) + U$ changes only due to the external pressure, $\dot{E} = -p_{ext} \bar{A}P/m$, which by virtue of (4) results in the internal energy balance

$$\dot{U} = -\frac{\bar{p} \bar{A} P}{m} \quad (15)$$

Comparing the dynamic Eqs. (4) and (15) with the form (6a, 6b) one finds $\mathbf{A} = \mathbf{1}$, \mathbf{C} equals the right hand side of Eqs. (4) and (15), $\mathbf{B} = \partial S / \partial \mathbf{x}_{RTD}$, and $\mathbf{D} = 0$. According Liu's Eq. (7a) we therefore find $\mathbf{A} = \partial S / \partial \mathbf{x}_{RTD}$, and the reduced dissipation inequality (7b) becomes

$$\begin{aligned} \bar{A}P/m \left(-\bar{p} \frac{\partial S}{\partial U} + (1-\kappa_V) \frac{\partial S}{\partial V_1} + \kappa_V \frac{\partial S}{\partial V_s} + \kappa_A \frac{\partial S}{\partial A} + \kappa_L \frac{\partial S}{\partial L} \right) \\ + \frac{\partial S}{\partial P} (-\partial_z V + \bar{A}(\bar{p} - p_{ext})) \\ + \Upsilon_V \left(\frac{\partial S}{\partial V_s} - \frac{\partial S}{\partial V_1} + \hat{\rho} \frac{\partial S}{\partial M_s} - \hat{\rho} \frac{\partial S}{\partial M_1} \right) \\ + \Upsilon_A \frac{\partial S}{\partial A} + \Upsilon_L \frac{\partial S}{\partial L} + \Upsilon_N \frac{\partial S}{\partial N} \geq 0 \end{aligned} \quad (16)$$

This reduced dissipation inequality has to be valid also in the absence of phase transformations, i.e. $\Upsilon_V = \Upsilon_A = \Upsilon_L = \Upsilon_N = 0$, and for arbitrary external pressure. Therefore, one finds that the entropy can not depend on the momentum of the piston, $\partial S / \partial P = 0$. Because the inequality has to be satisfied also for arbitrary sign of the momentum of the piston, one concludes that the expression in the braces of

Table 1
Variables and potentials for the different thermodynamic methods as used in this study

Method	Variables		Potentials
	Internal	External	
Rational Nonequilibrium Thermodynamics.	$\mathbf{x}_{\text{RTD}} = (P, U) \oplus \mathbf{X}_t$	–	$S = S(\mathbf{x}_{\text{RTD}})$
Matrix Model	$\mathbf{x}_{\text{MM}} = \mathbf{X}_t$	\dot{z}, T	$F = F(T; \mathbf{x}_{\text{MM}})$
GENERIC	$\mathbf{x}_{\text{GEN}} = (P, T) \oplus \mathbf{X}_t$	–	$E = E(\mathbf{x}_{\text{GEN}})$ $S = S(\mathbf{x}_{\text{GEN}} \setminus P)$

Variables that are externally controlled are separated from internal variables, for which the corresponding method models dynamic equations.

the first term must be zero, which amounts to the following constitutive relation for the multiphase pressure:

$$\bar{p} = \left(\frac{\partial S}{\partial U} \right)^{-1} \left((1 - \kappa_V) \frac{\partial S}{\partial V_1} + \kappa_V \frac{\partial S}{\partial V_s} + \kappa_A \frac{\partial S}{\partial A} + \kappa_L \frac{\partial S}{\partial L} \right) \quad (17)$$

for an arbitrary entropy function $S(U, \mathbf{X}_t)$.

As seen in the above discussion for rational nonequilibrium thermodynamics, the constitutive expression for the multiphase pressure \bar{p} resulted from studying the terms proportional to $\bar{A}P/m$. In the language of the Matrix Model and GENERIC, these are the reversible contributions. In order to apply the Matrix Model, one notices that the external rate \dot{x}_e in the present case is the velocity of the piston, and the choice of variables to describe the subsystem are given by (3),

$$\dot{x}_e = \dot{z}, \quad (18a)$$

$$\mathbf{x}_{\text{MM}} = \mathbf{X}_t \quad (18b)$$

Since the Matrix Model does not take into account thermal effects, one can either assume isothermal or adiabatic conditions. In the former case, the Helmholtz free energy F is the appropriate potential to calculate the thermodynamic forces F_x ; in the latter case it is the internal energy U . For simplicity, we choose here to look at the crystallization model as being isothermal. The thermodynamic forces are therefore

$$F_x = \left(\frac{\partial F}{\partial \mathbf{x}_{\text{MM}}} \right)_T \quad (19)$$

Considering the reversible terms in the evolution Eqs. (4b–4h) proportional to the piston speed $P/m = \dot{z} = \dot{x}_e$, one finds for the matrix in Eq. (9)

$$\mathbf{A}^T = \bar{A}(0, 0, 1 - \kappa_V, \kappa_V, \kappa_A, \kappa_L, 0) \quad (20)$$

Due to the antisymmetry of the reversible contributions in the Matrix Model, the expression for the multiphase pressure

can be recovered,

$$\begin{aligned} -\frac{1}{\bar{A}} F_e = \bar{p} &= -\frac{1}{\bar{A}} \mathbf{A}^T \circ \left(\frac{\partial F}{\partial \mathbf{x}_{\text{MM}}} \right)_T \\ &= - \left((1 - \kappa_V) \frac{\partial F}{\partial V_1} + \kappa_V \frac{\partial F}{\partial V_s} + \kappa_A \frac{\partial F}{\partial A} + \kappa_L \frac{\partial F}{\partial L} \right) \end{aligned} \quad (21)$$

The GENERIC formulation, contrary to the Matrix Model, includes also the dynamics of the piston similar to the rational thermodynamics treatment. On the other hand, contrary to the latter and similar to the former, GENERIC splits reversible from irreversible contributions in the dynamic equations. The entire system is described by the set of variables

$$\mathbf{x}_{\text{GEN}} = (P, T) \oplus \mathbf{X}_t, \quad (22)$$

where \mathbf{X}_t is again defined by (3). It is important to note that this choice for the thermal variable, $x_{\text{th}} = T$, is not the only possibility. One could also have chosen the internal energy $x_{\text{th}} = U$, which is, however, less convenient as a measurable quantity when it comes to applications. In the rational thermodynamics treatment, the choice $x_{\text{th}} = U$ is dictated by it being the appropriate variable for the entropy function, which on its turn is the appropriate potential in situations without heat exchange. In the GENERIC treatment, the system is thermally isolated as well. However, due to the use of two generators, namely total energy E and entropy S , one has significantly more freedom in choosing the set of variables. The consequences of this possibility and the relation to the other two descriptions will be discussed below. As far as the temperature equation is concerned, we write it in the general form

$$\dot{T} = \kappa_T \bar{A}P/m + (\vartheta_V \Upsilon_V + \vartheta_A \Upsilon_A + \vartheta_L \Upsilon_L + \vartheta_N \Upsilon_N), \quad (23)$$

in resemblance to (4b–4h), where κ_T mimics reversible compressibility effects and the terms $\vartheta_\mu \Upsilon_\mu$ ($\mu = V, A, L, N$) represent phase change contributions. It will be shown below that the degeneracy requirement (11a) determines κ_T , whereas (11b) will impose constraints on ϑ_μ ($\mu = V, A, L, N$).

Given the choice of variables (22), the next step is to specify the generators. We write

$$E = \frac{P^2}{2m} + V(z) + U(\mathbf{x}_{\text{GEN}} \setminus P) = \frac{P^2}{2m} + V(z) + U(T, \mathbf{X}_t), \quad (24a)$$

$$S = S(\mathbf{x}_{\text{GEN}} \setminus P) = S(T, \mathbf{X}_t), \quad (24b)$$

where we have assumed that neither the internal energy nor the entropy depend on the momentum of the piston. According to the GENERIC form (10), the reversible dynamics is driven by the energy gradient, of which the only velocity dependent component is $\partial E / \partial P = P/m = \dot{z}$. In order to capture the reversible terms in Eqs. (4b)–(4h) and (23), we propose that only the P -row and -column be non-zero, with

$$\begin{aligned} L_{P,*} &= -\bar{A}(0, \kappa_T, 0, 0, 1 - \kappa_V, \kappa_V, \kappa_A, \kappa_L, 0) \\ &\equiv (L_{P,P}, L_{P,T}, L_{P,\mathbf{X}_t}) \end{aligned} \quad (25)$$

The other elements can be completed by the anti-symmetry requirement for the entire matrix \mathbf{L} . This operator fulfills the Jacobi identity irrespective of the form of the unspecified entries if the latter are all independent of the momentum of the piston, P . The result of the Jacobi identity not constraining the compressibilities is in agreement with a detailed study of convection in a continuum multiphase field model [18].

For the evolution equation for the piston momentum according to (10), we may write by virtue of the degeneracy requirement (11a)

$$\begin{aligned} \dot{P} &= L_{P,*} \cdot \frac{\partial E}{\partial \mathbf{x}_{\text{GEN}}} - T L_{P,*} \cdot \frac{\partial S}{\partial \mathbf{x}_{\text{GEN}}} \\ &= L_{P,\mathbf{X}_t} \cdot \left(\frac{\partial E}{\partial \mathbf{X}_t} - T \frac{\partial S}{\partial \mathbf{X}_t} \right) = -\partial_z V(z) + L_{P,\mathbf{X}_t} \cdot \frac{\partial F}{\partial \mathbf{X}_t}, \end{aligned} \quad (26)$$

where we have used the relation $\partial E / \partial T = T \partial S / \partial T$ from the first to the second line and the definition of the Helmholtz free energy, $F \equiv U - TS$. If one identifies the last term in Eq. (26) with the force $\bar{A} \bar{p}$ according to (4a), one recovers exactly the same expression for the multiphase pressure \bar{p} as found for the Matrix Model in (21) when using the explicit form for the reversible operator (25).

The above derivation highlights the importance of the degeneracy requirement (11a) in this particular example. One started with choosing the temperature as the thermal variable, whereas none of the two generators is the appropriate thermodynamic potential to that variable, i.e. the individual generators do not contain the full thermodynamic information. Only through their combination by way of the degeneracy requirement for the reversible operator they are combined into the Helmholtz free energy, which on its turn indeed is the appropriate thermodynamic potential to these variables.

Last but not least, the degeneracy requirement (11a) for the entropy imposed on this system,

$$\kappa_T \frac{\partial S}{\partial T} + (1 - \kappa_V) \frac{\partial S}{\partial V_1} + \kappa_V \frac{\partial S}{\partial V_s} + \kappa_A \frac{\partial S}{\partial A} + \kappa_L \frac{\partial S}{\partial L} = 0 \quad (27)$$

allows one to determine the function κ_T appearing in the temperature Eq. (23), if the entropy $S = S(T, \mathbf{X}_t)$ and the other functions $\kappa_V, \kappa_A, \kappa_L$ are known. This completes the formulation of all nondissipative contributions to the dynamic equations.

Finally, the relation between the pressure expression (17) obtained from the rational thermodynamics treatment and the result (21) for the Matrix Model and GENERIC formulations is discussed. It is straightforward to show that both results are identical for

$$\left(\frac{\partial S(U, \mathbf{X}_t)}{\partial U} \right)^{-1} \frac{\partial S(U, \mathbf{X}_t)}{\partial \mathbf{X}_t} = - \frac{\partial F(T, \mathbf{X}_t)}{\partial \mathbf{X}_t}, \quad (28)$$

which is fulfilled due to the very definition of the Helmholtz free energy with $1/T \equiv \partial S / \partial U$. In conclusion, all three thermodynamic methods lead to the same constitutive expression for the multiphase pressure \bar{p} , although along different routes. The result emphasizes the close relation between the compressibilities for the structural variables, $(1 - \kappa_V, \kappa_V, \kappa_A, \kappa_L)$, and the way they appear in the expression for \bar{p} in combination with their conjugate variables. It is noteworthy, however, that none of the three thermodynamic methods constrains the functional form of the compressibilities in terms of the variables $(x_{\text{th}}, \mathbf{X}_t)$. Thus, it is only one's physical understanding of the system which determines these functions, e.g. $\kappa_V = \kappa_A = \kappa_L = 0$ for a completely incompressible solid phase.

In order to complete the discussion of the nondissipative dynamics we focus again on the momentum balance Eq. (4a), and on the forces and pressures appearing therein. Although the introduction of a potential force is sufficient to drive the piston against the internal multiphase pressure and to describe the physics of interest here, the external pressure p_{ext} was used in addition for the rational thermodynamics treatment in order to conclude that the entropy does not depend on the momentum of the piston, i.e. $\partial S / \partial P = 0$. Since the GENERIC formalism is valid for isolated systems, external pressures cannot be captured. On the other hand, the Matrix Model does not model the momentum balance at all since this method explicitly deals with driven systems. So, the way in which the piston speed, $\dot{z} = P/m$, is generated is of no interest there, but it rather describes how the internal system reacts to a given piston speed, namely it gives a relation for the force on the piston.

A summary of the reversible effects is given in Fig. 2. A non-zero piston velocity changes the morphological variables, which in their turn, through the thermodynamic potential, are related to changes in the corresponding intensive variables. These, in particular the altered pressures, also change the multiphase pressure on the piston, which closes the loop of reversible events.

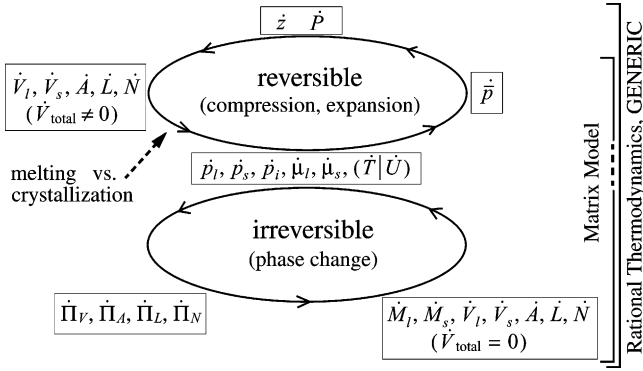


Fig. 2. Overview of reversible and irreversible effects and their mutual coupling upon changing the position of the piston. Symbols as introduced in the text.

4.3. Driving forces for phase change

The thermodynamic driving forces for phase change are examined in this section, and the results for the three thermodynamic approaches are compared. In order to simplify the notation, it is useful to rewrite the phase change contributions. Irrespective of whether one considers the rational thermodynamics (4a–4h, 15), Matrix Model (4b–4h), or the GENERIC treatment (4a–4h, 23), the phase change contributions to these equations can always be written in the form [1]

$$\dot{\mathbf{x}}|_{\text{pc}} = \mathbf{a}_V \Upsilon_V + \mathbf{a}_A \Upsilon_A + \mathbf{a}_L \Upsilon_L + \mathbf{a}_N \Upsilon_N, \quad (29)$$

if \mathbf{x} denotes the set dynamic variables required for a particular thermodynamic method, as listed in Table 1. By virtue of the dynamic equations for the structural variables (4e–4h), one finds with Eq. (29) for the last four components of the vectors \mathbf{a}_μ ($\mu = V, A, L, N$)

$$\begin{aligned} \mathbf{a}_{V,V_s} &= 1 & \mathbf{a}_{A,V_s} &= 0 & \mathbf{a}_{L,V_s} &= 0 & \mathbf{a}_{N,V_s} &= 0 \\ \mathbf{a}_{V,A} &= 0 & \mathbf{a}_{A,A} &= 1 & \mathbf{a}_{L,A} &= 0 & \mathbf{a}_{N,A} &= 0 \\ \mathbf{a}_{V,L} &= 0 & \mathbf{a}_{A,L} &= 0 & \mathbf{a}_{L,L} &= 1 & \mathbf{a}_{N,L} &= 0 \\ \mathbf{a}_{V,N} &= 0 & \mathbf{a}_{A,N} &= 0 & \mathbf{a}_{L,N} &= 0 & \mathbf{a}_{N,N} &= 1 \end{aligned} \quad (30)$$

It is important to note that these four vectors are linearly independent, as is apparent above. The set of four vectors \mathbf{a}_μ ($\mu = V, A, L, N$) differ between the three thermodynamic formulations in that not all of them include P in the set of variables, and different choices for the thermal variable x_{th} are made. With these vectors, e.g. the expression $\mathbf{a}_V \Upsilon_V$ captures the phase change contributions due to volume change in all dynamic equations. The formulation of the phase change contributions can thus concentrate on finding constitutive relations for the “fluxes” Υ_μ ($\mu = V, A, L, N$).

The rational nonequilibrium thermodynamics treatment of the phase change contributions is inherently linked to the determination of the reversible contributions. Starting from the reduced dissipation inequality (16), one uses the results

that the entropy does not depend on the momentum of the piston as well as the relation (17) for the multiphase pressure, leading to

$$\sum_{\mu=V,A,L,N} \Upsilon_\mu \Pi_\mu^{\text{(RTD)}} \equiv \sum_{\mu=V,A,L,N} \Upsilon_\mu \left(\mathbf{a}_\mu^{\text{(MM)}} \cdot \frac{\partial S(U, \mathbf{X}_t)}{\partial \mathbf{X}_t} \right) \geq 0, \quad (31)$$

where we have used the fact that the P - and U -components of all vectors $\mathbf{a}_\mu^{\text{(RTD)}}$ ($\mu = V, A, L, N$) are zero by virtue of the dynamic Eqs. (4a) and (15), i.e. one can use $\mathbf{a}_\mu^{\text{(RTD)}} = (0, 0, \mathbf{a}_\mu^{\text{(MM)}})$ ($\mu = V, A, L, N$). This inequality (31) has the form of a relationship between fluxes, Υ_μ , and thermodynamic forces, $\Pi_\mu^{\text{(RTD)}}$. For the comparison of this result with the results for the other two thermodynamic procedures it is essential that this criterion (31) is a scalar equation, i.e. a single constraint on the phase change dynamics.

The Matrix Model and GENERIC enforce the dissipation inequality by imposing certain requirements on operators, which is a much stronger constraint than the reduced dissipation inequality (7b). The consequences of this difference will become clear in the following.

Considering frictionless motion of the piston amounts in the Matrix Model to setting $\eta = 0$, because then $F_e|_{\text{diss}} = \eta \dot{z} = 0$. The remaining irreversible contributions are due to phase change; these effects are captured by the matrix β in the Matrix Model (9),

$$\dot{\mathbf{x}}_{\text{MM}}|_{\text{pc}} = \sum_{\mu=V,A,L,N} \mathbf{a}_\mu^{\text{(MM)}} \Upsilon_\mu = \beta \circ \left(-\frac{\partial F}{\partial \mathbf{x}_{\text{MM}}} \right)_T, \quad (32)$$

where we have used the expression (19) for the thermodynamic force. It can be shown rigorously that due to the positive semi-definiteness and symmetry of the operator β , it must be of the form

$$\beta = \sum_{\substack{\nu=V,A,L,N \\ \mu=V,A,L,N}} R_{\mu\nu} \mathbf{a}_\mu^{\text{(MM)}} \mathbf{a}_\nu^{\text{(MM)T}}, \quad (33)$$

with

$$\mathbf{R}^T = \mathbf{R}, \quad \mathbf{R} \geq \mathbf{0} \quad (34)$$

This result is based on the fact that the four vectors $(\mathbf{a}_V, \mathbf{a}_A, \mathbf{a}_L, \mathbf{a}_N)$ are linearly independent, as the components displayed in Eq. (30) show.

A very similar result is obtained from the GENERIC method. There, the irreversible contributions are captured by the second term on the right side of Eq. (10), i.e. a positive semi-definite and symmetric matrix \mathbf{M} has to be determined to model the phase change contributions

$$\begin{aligned} \dot{\mathbf{x}}_{\text{GEN}}|_{\text{pc}} &= \sum_{\mu=V,A,L,N} \mathbf{a}_\mu^{\text{(GEN)}} \Upsilon_\mu \\ &= \mathbf{M} \cdot \left(\frac{\partial S}{\partial \mathbf{x}_{\text{GEN}}} - \frac{1}{T} \frac{\partial E}{\partial \mathbf{x}_{\text{GEN}}} \right), \end{aligned} \quad (35)$$

where we have used the degeneracy requirement $\mathbf{M} \cdot \partial E / \partial \mathbf{x}_{\text{GEN}} = \mathbf{0}$. Similarly to the Matrix Model, it can be shown that the irreversible operator must be of the form

$$\mathbf{M} = \sum_{\substack{\nu=V,A,L,N \\ \mu=V,A,L,N}} R_{\mu\nu} \mathbf{a}_{\mu}^{(\text{GEN})} \mathbf{a}_{\nu}^{(\text{GEN})\text{T}}, \quad (36)$$

with

$$\mathbf{R}^{\text{T}} = \mathbf{R}, \quad \mathbf{R} \geq \mathbf{0} \quad (37)$$

The last of the GENERIC requirements on \mathbf{M} given in (36), in addition to the symmetry and positive semi-definiteness, is the degeneracy requirement (11b). Multiplication of (36) with the energy gradient leads to a complicated, general relation. If \mathbf{R} is strictly positive, one can show that the full degeneracy requirement is mathematically equivalent to

$$\mathbf{a}_{\mu}^{(\text{GEN})} \cdot \frac{\partial E(T, \mathbf{X}_t)}{\partial \mathbf{X}_t} = 0, \quad \mu = V, A, L, N \quad (38)$$

In the following, this result will be used even if \mathbf{R} is positive semi-definite only, although it is not mathematically rigorous in that case. Furthermore, it has been shown for spherulitic growth that the elements of a positive semi-definite matrix \mathbf{R} take peculiar, unphysical values if Eqs. (38) are not enforced [1]. The conditions (38) can be used to determine the functions $\vartheta_{\mu} (\mu = V, A, L, N)$, which appear in the phase change contributions of the temperature Eq. (23). To finally get the phase change contributions of the GENERIC formulation, one evaluates the expression (35) using $\partial E / \partial T = T \partial S / \partial T$ and $F = U - TS$. One finds that the GENERIC phase change contributions are identical to the result obtained with the Matrix Model, which for both methods can be expressed as

$$\begin{aligned} \Upsilon_{\mu} &= \sum_{\nu=V,A,L,N} R_{\mu\nu} \left(-\frac{1}{T} \mathbf{a}_{\nu}^{(\text{MM})} \cdot \frac{\partial F(T, \mathbf{X}_t)}{\partial \mathbf{X}_t} \right) \\ &\equiv \sum_{\nu=V,A,L,N} R_{\mu\nu} \Pi_{\nu}^{(\text{MM,GEN})}, \quad \mu = V, A, L, N \end{aligned} \quad (39)$$

This relation again relates the fluxes, Υ_{μ} , to the thermodynamic forces, $\Pi_{\mu}^{(\text{MM,GEN})}$.

Let us now discuss the relation between the results obtained from the rational thermodynamics treatment (31) and the main conclusion from the Matrix Model and GENERIC formulation (39). Due to the definition of the Helmholtz free energy $F = U - TS$ with $1/T \equiv \partial S / \partial U$, one finds that the thermodynamic driving forces for phase change are identical, i.e. $\Pi_{\mu}^{(\text{RTD})} = \Pi_{\mu}^{(\text{MM,GEN})} \equiv \Pi_{\mu} \forall \mu$. The difference between the two results (31) and (39) concerns to what extent the dynamics is constrained by thermodynamic principles. Whereas Eq. (31) can be recovered from Eq. (39), the inverse construction does not hold. Therefore, the form (39) contains more structure which is not inherent to the result (31). As a specific example of this difference one may consider the case in which the thermodynamic potential does not depend on the variable L , as is often the case in simplified

models, which results in $\Pi_L = 0$. In rational thermodynamics, this deletes the flux Υ_L from the dissipation inequality (31), which leaves it completely unconstrained by thermodynamic principles. In the Matrix Model and GENERIC treatment, setting one of the driving forces does not allow for a free choice of the flux Υ_L . This point will be illustrated further in the following section, in which the above general results are applied to a specific choice for the thermodynamic potential.

4.4. A specific example

All of the above results, in particular for the multiphase pressure \bar{p} and for the phase change contributions, Υ_{μ} , and their driving forces, Π_{μ} ($\mu = V, A, L, N$), have been discussed for an arbitrary thermodynamic potential. It has been shown that the results (21, 31, 39) can be expressed in terms of the Helmholtz free energy, irrespective of the thermodynamic formalism used. To illustrate the meaning of these results further, we make a specific choice for the Helmholtz free energy, namely,

$$\begin{aligned} F(T, \mathbf{X}_t) &= F_l(T, M_l, V_l) + F_s(T, M_s, V_s) + F_i(T, A) \\ &\quad - TS_{\text{cfg}}(N, V_l, V_s), \end{aligned} \quad (40)$$

which is the sum of the Helmholtz free energies of the liquid, solid, and interface, and also includes a configurational entropy for the crystals, S_{cfg} , e.g. of the Van der Waals type. For the partial derivatives with respect to \mathbf{X}_t one obtains

$$\begin{aligned} \left(\frac{\partial F}{\partial \mathbf{X}_t} \right)_T &= \left(\mu_l, \mu_s, -p_l - T \frac{\partial S_{\text{cfg}}}{\partial V_l}, -p_s - T \frac{\partial S_{\text{cfg}}}{\partial V_s}, \right. \\ &\quad \left. \sigma, 0, T \frac{\partial S_{\text{cfg}}}{\partial N} \right), \end{aligned} \quad (41)$$

with chemical potentials μ_l, μ_s , bulk pressures p_l, p_s , and where σ denotes the surface tension given by $\sigma = -p_i = \partial F_i / \partial A$. This gives the following expression for the multiphase pressure (21) on the piston:

$$\begin{aligned} \bar{p} &= (1 - \kappa_V) \left(p_l + T \frac{\partial S_{\text{cfg}}}{\partial V_l} \right) + \kappa_V \left(p_s + T \frac{\partial S_{\text{cfg}}}{\partial V_s} \right) \\ &\quad - \kappa_A \sigma, \end{aligned} \quad (42)$$

highlighting again the relation between the reversible effects in Eqs. (4d–4h) and the conjugate variables. In the absence of excluded volume the configurational entropy depends only on the total volume, $V_{\text{total}} = V_l + V_s$, rather than on the volumes individually. Then, the configurational contributions in the multiphase pressure sum up to $T(\partial S / \partial V_{\text{total}})|_N$, which includes also the case on an ideal gas of crystallites.

The driving forces for phase change, Π_{μ} (31,39), for the specific Helmholtz free energy (40) become

$$\begin{pmatrix} \Pi_V \\ \Pi_A \\ \Pi_L \\ \Pi_N \end{pmatrix} = \frac{1}{T} \begin{pmatrix} \hat{\rho}(\mu_l - \mu_s) + p_s - p_l + T \left(\frac{\partial S_{\text{cfg}}}{\partial V_s} - \frac{\partial S_{\text{cfg}}}{\partial V_l} \right) \\ -\sigma \\ 0 \\ T \frac{\partial S_{\text{cfg}}}{\partial N} \end{pmatrix} \quad (43)$$

Apart from the surface tension and the configurational entropy contributions, the driving force Π_V is equal to the Helmholtz free energy transfer as a unit volume changes phase. Note that this is not equal to the difference in Helmholtz free energies per unit volume since in general $\hat{\rho} \neq \rho_s$ and $\hat{\rho} \neq \rho_l$ ($\rho_k := M_k/V_k$, $k = l, s$). The relevance of the Helmholtz free energy for this process rather than another thermodynamic potential originates from the fact that the phases have been assumed to be at equal temperatures.

Let us now discuss different choices for the mass transfer coefficient $\hat{\rho}$, which is still undetermined. For equal mass densities, i.e. $\rho_l = \rho_s$, $\hat{\rho}$ is most naturally chosen equal to this mass density. However, for $\rho_l \neq \rho_s$ the expression of $\hat{\rho}$ is more complicated. One might choose $\hat{\rho}^{-1} = 1/2(\rho_l^{-1} + \rho_s^{-1})$, or also $\hat{\rho}^{-1} = \phi_s \rho_l^{-1} + \phi_l \rho_s^{-1}$ with the volume fractions $\phi_k \equiv V_k/(V_l + V_s)$ (see [19] for more details). A further choice is the following. In the system studied here the phases have different pressures, p_l and p_s . If the pressure difference is relatively small, one might expand the chemical potentials to get

$$\begin{aligned} & \hat{\rho}[\mu_l(T, p_l) - \mu_s(T, p_s)] - p_l + p_s \\ & \simeq \hat{\rho}[\mu_l(T, p^*) - \mu_s(T, p^*)] \\ & + (p_s - p_l) \left[1 - \hat{\rho} \left(\frac{1/2 + \varepsilon}{\rho_l} + \frac{1/2 - \varepsilon}{\rho_s} \right) \right], \quad (44) \end{aligned}$$

where the chemical potentials are evaluated at equal pressure $p^* \equiv (p_l + p_s)/2 + \varepsilon$. One can then choose $\hat{\rho}$ such that the terms on the third line vanish, which can be considered a physically reasonable choice as long as $\hat{\rho}$ is between the mass densities of the single phases. As far as the parameter ε is concerned, it is desirable to evaluate the driving force for phase change at the experimentally measurable pressure \bar{p} , i.e. one would then set ε such that $p^* = \bar{p}$.

On the one hand, the appearance of chemical potential differences and pressure difference in the driving forces (43) can be appreciated physically already at this stage. On the other hand, however, the significance of the surface tension and the configurational entropy contributions will become clear only after discussing the possible choices for the matrix \mathbf{R} in Eq. (39) in the following section, which is needed for relating the phase change fluxes to the thermodynamic forces.

4.5. Discussion of morphological details

The importance of making a good choice for the morphological variables has been emphasized in Section 2.1. We

are now in the position to elaborate on that point in more detail. It is discussed in this section how physically important effects such as impingement of crystals, depletion zones around crystals, and shape recognition is possible within the model developed here, without violating thermodynamic principles. All these effects will be discussed in terms of appropriate choices for the matrix \mathbf{R} in the force-flux relation (39) obtained from the Matrix Model and GENERIC treatment. To what extent the results can also be used within the rational thermodynamic treatment will be discussed below. It is important to notice that this entire section deals with the thermodynamic contributions to the phase change dynamics, i.e. the proper combination of the driving forces Π_μ ($\mu = V, A, L, N$). It does not discuss the kinetic prefactors of the process, namely, time scales entering as prefactors are not constrained by this discussion.

4.5.1. Impingement

As discussed in Section 2.1, the Minkowski functionals for the union of grains differ from the sums of the single-grain Minkowski functionals if grains do overlap. Consider the solid phase as a sum of overlapping convex crystals as shown in Fig. 1. Then, the sum of the single-grain Minkowski functionals are the sum of the volumes, V_Σ , the sum of the surfaces, A_Σ , the sum of the average mean curvatures, L_Σ , and the sum of the connectivities, N_Σ , the last simply reducing to the number of crystals. These variables are desirable for studying nucleation and growth processes, where the nucleation rate changes N_Σ and the change in V_Σ finally describes the growing crystals. However, these variables need to be related to the variables (V_s, A, L, N) included in Eqs. (2) and (3). While we have already chosen $L = L_\Sigma$ and $N = N_\Sigma$ from the beginning in Section 2.1, the relationships between the volumes, V_s and V_Σ , and the surfaces, A and A_Σ , are not straightforward. It again proves fruitful to resort to integral geometry, where the study of randomly positioned and randomly oriented overlapping convex grains is ubiquitous [12–16]: it is called the Boolean Grain Model. One finds the following relations, also derived by Avrami [20], between the physical volume and surface, V_s and A , on the one hand and the quantities V_Σ and A_Σ on the other hand:

$$V_s = V_{\text{total}} \left(1 - \exp \left(- \frac{V_\Sigma}{V_{\text{total}}} \right) \right), \quad (45a)$$

$$A = A_\Sigma \exp \left(- \frac{V_\Sigma}{V_{\text{total}}} \right), \quad (45b)$$

where V_{total} denotes the total volume under consideration. As far as phase change dynamics is concerned, this total volume is constant as shown in Section 4.1.

What is the consequence of the two relations (45a and b) on the phase change dynamics? For a given nucleation rate per unit volume, $\alpha(t)[\text{m}^{-3}\text{s}^{-1}]$, one can express

$$V_\Sigma(t) = V_{\text{total}} \left(\int_{-\infty}^t \alpha(t') v_s(t', t) dt' \right), \quad (46)$$

where $v_s(t', t)$ denotes the volume at time t of a single crystallite which began to grow from a nucleus at time t' . If the growth of a spherical crystallite is described by a radial growth rate $G(t)$, its volume is related to its radius,

$$R(t', t) = \int_{t'}^t G(s) ds, \quad (47)$$

by $v_s(t', t) = 4\pi/3 R^3(t', t)$. Using the relations (45a,45b,46), one finds after successive differentiation of the integral the following coupled so-called differential Schneider rate equations [21],

$$\dot{V}_s(t) = G(t)A(t), \quad (48a)$$

$$\dot{A}(t) = G(t)\mathcal{L}(t), \quad (48b)$$

$$\dot{L}(t) = 8\pi G(t)N(t) \quad (48c)$$

$$\dot{N}(t) = \alpha_{\text{eff}}(t)V_{\text{total}} \quad (48d)$$

with (see [1] for more details)

$$\mathcal{L} \equiv (V_{\text{total}} - V_s) \left[L - \left(\frac{A}{V_{\text{total}} - V_s} \right)^2 \right], \quad (49a)$$

$$L(t) \equiv V_{\text{total}} \left(\int_{-\infty}^t \alpha(t') 8\pi R(t', t) dt' \right), \quad (49b)$$

and with $\alpha_{\text{eff}} = \alpha$ for overlapping crystals.

The fact that the model studied here combines properties that do consider crystal overlap (V_s and A) with other properties that do not account for overlap (L and N) brings about the complicated function \mathcal{L} . If one would study a system of non-overlapping crystals, the proper choice of variables is given by $V_s = V_\Sigma$ and $A = A_\Sigma$ and one would find $\mathcal{L} = L$.

A further distinction between overlapping and non-overlapping crystals is how to account for the generation of so-called phantom nuclei, i.e. nuclei that are generated in an area already covered by the crystalline phase. It has been shown that for the Boolean Grain Model of overlapping crystals, the crystalline volume and surface as computed from Eqs. (48) include this effect correctly [20], i.e. one does not need to correct for phantom nuclei if impingement is accounted for. However, it must be realized that N as determined from Eq. (48d) indeed does include phantom nuclei. For non-overlapping crystals one has to replace the nucleation rate $\alpha_{\text{eff}} = \alpha$ in Eq. (48d) by $\alpha_{\text{eff}} = \alpha(1 - V_s/V_{\text{total}})$ in order to exclude the counting of phantom nuclei in N as well as their effect on V_s , A , L . Thus, the distinction between overlapping and non-overlapping crystals reduces to choosing the functions \mathcal{L} in the evolution Eq. (48b) and the effective nucleation rate α_{eff} in Eq. (48d).

The effects of impingement as discussed above are now incorporated into the thermodynamic model developed here. One notes that the right hand side of the Schneider rate Eq. (48) must be of the form (39) according to the Matrix Model and the GENERIC procedure. Since the same radial growth rate appears in the Eqs. (48a)–(48c), the first three

rows in the matrix \mathbf{R} are proportional to each other, with their third column entries undetermined because $\Pi_L = 0$ in (43). As a consequence of the symmetry requirement one finds that the matrix \mathbf{R} can be written in the form

$$\mathbf{R}_{\text{sphere}} = \begin{pmatrix} A\mathbb{X} & \mathcal{L}\mathbb{X} & 8\pi N\mathbb{X} & AZ \\ \mathcal{L}\mathbb{X} & \frac{\mathcal{L}^2}{A}\mathbb{X} & 8\pi \frac{N\mathcal{L}}{A}\mathbb{X} & \mathcal{L}Z \\ 8\pi N\mathbb{X} & 8\pi \frac{N\mathcal{L}}{A}\mathbb{X} & \frac{(8\pi N)^2}{A}\mathbb{X} & 8\pi NZ \\ AZ & \mathcal{L}Z & 8\pi NZ & \mathbb{Y} \end{pmatrix} \quad (50)$$

The matrix contains three parameters, (\mathbb{X} , \mathbb{Y} , \mathbb{Z}), which are constrained by the requirement $\mathbf{R} \geq \mathbf{0}$. Due to $A \geq 0$ for physical reasons, one finds that the positivity requires $\mathbb{X} \geq 0$ and $\mathbb{Y} \geq 0$. Whereas the diagonal blocks with the parameters \mathbb{X} and \mathbb{Y} affect only the growth or nucleation, respectively, the off-diagonal blocks with the parameter \mathbb{Z} lead to a coupling of nucleation and growth. The nucleation and growth rate are physically different phenomena, which is reflected in the rank of the matrix expression (50) being equal to two. One should note, however, that for the choice $\mathbb{X}\mathbb{Y} = A\mathbb{Z}^2$, the rank drops to one, and the nucleation and growth rate are proportional [1], which is exactly the isokinetic assumption inherent to the Nakamura equation [22]. In the general case, one concludes from Eq. (50) that in the Matrix Model and the GENERIC treatment, the flux Υ_L is determined in the same way as Υ_V and Υ_A , with the radial growth rate

$$G_{\text{sphere}} = \mathbb{X} \left(\Pi_V + \frac{\mathcal{L}}{A} \Pi_A \right) + \mathbb{Z} \Pi_N \quad (51)$$

To examine the application of this result to the rational thermodynamics treatment, one can rewrite the dissipation inequality (31) into a form similar to (39) with a positive matrix and all L -components deleted due to $\Pi_L = 0$. If one additionally assumes the matrix to be symmetric and uses the same procedure as described just above, one finds the matrix (50) with all L -components deleted. Therefore, the radial growth rate for the rational thermodynamic treatment with the additional symmetry requirement is also given by Eq. (51), whereas no constraints are imposed on the flux Υ_L , in contrast to the result for the Matrix Model and for GENERIC. Whereas the term Π_V in Eq. (51) includes bulk contributions similarly found elsewhere [1,19,23], the surface tension term, $\Pi_A = -\sigma/T$, nicely shows the size-dependence of the growth rate in terms of the inverse length scale \mathcal{L}/A . The expression (50) also highlights again where impingement effects are introduced: First, in the choice of the function \mathcal{L} as appearing in Eq. (50) either of the form (49a) or simply as $\mathcal{L} = L$, and second, in the expression for the effective nucleation rate α_{eff} as discussed above, where $\alpha_{\text{eff}} V_{\text{total}} = \sum_v R_{Nv} \Pi_v$ according to Eq. (39).

4.5.2. Depletion zones

Depending on the physical system under consideration, a depletion zone might develop around the crystal which

makes it impossible for new nucleation to occur in that region. In multicomponent diffusion-controlled systems, a certain element critical for the nucleation might not be sufficiently available in the vicinity of the growth front of other crystals. In the following, we denote the thickness of the depletion zone by d , which may be an arbitrary function of the system variables \mathbf{x} . We do not consider impingement for the simplicity of the argument, i.e. $V_s = V_\Sigma$ and $A = A_\Sigma$. The depletion zone affects only the nucleation rate. The volume available for nucleation is the total volume minus the volume of the crystals including their d -surrounding (see also [24]). For spherulitic growth, the latter is given by Eqs. (46) and (47) with

$$\begin{aligned} V_{\Sigma,d} &= V_{\text{total}} \left(\int_{-\infty}^t \alpha(t') \frac{4\pi}{3} (R(t', t) + d)^3 dt \right) \\ &= V_\Sigma + dA_\Sigma + \frac{1}{2}d^2L_\Sigma + \frac{4\pi}{3}d^3N_\Sigma \end{aligned} \quad (52)$$

by expanding the polynomial. Thus, all four structural variables, $(V_\Sigma, A_\Sigma, L_\Sigma, N_\Sigma)$, are needed to express the effective nucleation rate, which is given by $\alpha_{\text{eff}} = \alpha(1 - V_{\Sigma,d}/V_{\text{total}})$. The incorporation of the depletion zone effect into the thermodynamic model discussed here enters into the evaluation of the nucleation rate expression $\alpha_{\text{eff}}V_{\text{total}} = \sum_\nu R_{N\nu}\Pi_\nu$ according to Eq. (39).

4.5.3. Shape recognition

Instead of spherulites, let us finally also consider the growth of disks of thickness h , also called lamellae in polymer crystallization, without consideration of impingement. It is assumed that h is constant with respect to the phase change dynamics. In other words, we attempt to study two-dimensional growth, in contrast to the three-dimensional growth for spherulites. With the volume of a single disk,

$$v_s^{(d)}(t', t) = \pi h R^2(t', t), \quad (53)$$

one finds, after successive differentiation of the total crystal volume (46), the four dynamic equations

$$\dot{V}_\Sigma^{(d)}(t) = G(t)A_\Sigma^{(d)}(t), \quad (54a)$$

$$\dot{A}_\Sigma^{(d)}(t) = G(t)L_\Sigma^{(d)}(t), \quad (54b)$$

$$\dot{L}_\Sigma^{(d)}(t) = 2\pi h \alpha_{\text{eff}}(t) V_{\text{total}} \quad (54c)$$

$$\dot{N}_\Sigma(t) = \alpha_{\text{eff}}(t) V_{\text{total}}, \quad (54d)$$

with $V_\Sigma^{(d)}$ the total crystalline volume. According to Eq. (46), the surface of the growth faces is

$$A_\Sigma^{(d)}(t) := V_{\text{total}} \left(\int_{-\infty}^t \alpha(t') 2\pi h R(t', t) dt \right), \quad (55)$$

N_Σ the number of disks, and $L_\Sigma^{(d)} := 2\pi h N_\Sigma$. Although $L_\Sigma^{(d)}$ is statically related to the number of disks in the phase change dynamics, this quantity still is to be kept in the set of variables since the thickness h does not necessarily have to

be constant in the reversible dynamics, i.e. under compression and expansion. To express the thickness of the disk in terms of the system variables, we replace $2\pi h$ in Eq. (54c) by $L_\Sigma^{(d)}/N_\Sigma$. It is crucial to realize that $A_\Sigma^{(d)}$ includes only the surface area of the growth faces, whereas the areas of the remaining two, non-growing surfaces can be expressed as

$$\begin{aligned} A_\Sigma^{(n)} &= V_{\text{total}} \left(\int_{-\infty}^t \alpha(t') 2\pi R^2(t', t) dt \right) = 2 \frac{V_\Sigma^{(d)}}{h} \\ &= 4\pi \frac{N_\Sigma}{L_\Sigma^{(d)}} V_\Sigma^{(d)} \end{aligned} \quad (56)$$

As a consequence, one might assign different surface tensions, σ , to the different areas, leading to a Helmholtz free energy expression for the surface contributions in Eq. (40) of the form

$$F_1(T, V_\Sigma^{(d)}, A_\Sigma^{(d)}, L_\Sigma^{(d)}, N_\Sigma) = \sigma^{(d)}(T)A_\Sigma^{(d)} + \sigma^{(n)}(T)A_\Sigma^{(n)}, \quad (57)$$

which by virtue of Eq. (56) depends on all four structural variables $(V_\Sigma^{(d)}, A_\Sigma^{(d)}, L_\Sigma^{(d)}, N_\Sigma)$. We therefore conclude that the thermodynamic driving forces defined through Eq. (39) are all non-zero, i.e. $\Pi_\mu \neq 0$ for $\mu = V, A, L, N$.

In order to formulate the planar growth mode of crystals described above by the thermodynamics model developed here, one notes again that the right hand side of the Schneider rate Eq. (54) must be of the form (39) according to the Matrix Model and the GENERIC procedure. Because the radial growth rate appears in both Eqs. (54a) and (54b), and the nucleation rate in Eqs. (54c) and (54d), respectively, the first and second row in the matrix \mathbf{R} must be proportional, and the third and fourth row must be proportional, respectively. Exploiting the symmetry property, one finally finds that the matrix must be of the form

$$\mathbf{R}_{\text{disk}} = \begin{pmatrix} A\mathbb{X} & L\mathbb{X} & \frac{AL}{N}\mathbb{Z} & A\mathbb{Z} \\ L\mathbb{X} & \frac{L^2}{A}\mathbb{X} & \frac{L^2}{N}\mathbb{Z} & L\mathbb{Z} \\ \frac{AL}{N}\mathbb{Z} & \frac{L^2}{N}\mathbb{Z} & \frac{L^2}{N^2}\mathbb{Y} & \frac{L}{N}\mathbb{Y} \\ A\mathbb{Z} & L\mathbb{Z} & \frac{L}{N}\mathbb{Y} & \mathbb{Y} \end{pmatrix}, \quad (58)$$

where we have omitted the superscript (d) and the subscript Σ to simplify the notation. The matrix contains three parameters, $(\mathbb{X}, \mathbb{Y}, \mathbb{Z})$, which again are constrained by the requirement $\mathbf{R} \geq \mathbf{0}$. Exactly as in the case for spherulites discussed above, one finds, first, $\mathbb{X} \geq 0$ and $\mathbb{Y} \geq 0$, second, that the diagonal blocks with the parameters \mathbb{X} and \mathbb{Y} affect only the growth and nucleation, respectively, whereas the off-diagonal blocks with the parameter \mathbb{Z} lead to a coupling of nucleation and growth. Third, the rank of the matrix equal to two represents the separation of nucleation and growth. And fourth, for the choice $\mathbb{X}\mathbb{Y} = A\mathbb{Z}^2$ the rank

drops to one, and the nucleation and growth rate are proportional [1], satisfying the isokinetic assumption inherent to the Nakamura equation [22]. The specific choice of these three parameters (\mathbb{X} , \mathbb{Y} , \mathbb{Z}) depends on the specific system under consideration and on the physics that shall be built into the dynamic model for phase transition. From the form (58) and the force-flux relation (39) one finds for the radial growth rate of the disk

$$G_{\text{disk}} = \mathbb{X} \left(\Pi_V + \frac{L}{A} \Pi_A \right) + \mathbb{Z} \left(\frac{L}{N} \Pi_L + \Pi_N \right) \quad (59)$$

This expression (59) looks formally similar to the radial growth rate of the sphere, G_{sphere} in Eq. (51), apart from the additional term in the non-constant thickness $2\pi h = L/N$. It is essential to realize, however, that the thermodynamic driving forces Π_μ ($\mu = V, A, L, N$) are different due to the surface contribution (57) in the Helmholtz free energy. Thus, spherulitic and disk-like growth differ, first, in the connection of the thermodynamic driving forces, Π_μ ($\mu = V, A, L, N$), to the single-phase properties through the thermodynamic potential, and second, in the form of the matrix \mathbf{R} . In other words, in general the different form of the Schneider rate Eqs. (48) and (54) also enters, by way of the symmetry property of the matrix, into how the thermodynamic forces are combined to give the fluxes. As far as the rational thermodynamic treatment is concerned, one gets the same result as above for the Matrix Model and the GENERIC formulation *only after making additional assumptions*. If the dissipation inequality (31) is rewritten in the form of a force-flux relation (39) with a positive matrix, one needs to require additionally that this matrix is symmetric, which is not ensured from within the rational thermodynamic treatment.

Fig. 2 offers an overview of the effects of phase change, irrespective of impingement, depletion zones, and crystal shape. As the single-phase pressures are changed due to a non-zero piston speed, they initiate the irreversible cycle by changing the driving forces for phase change as defined in Eq. (39). The driving forces then change the masses and morphological variables, i.e. the extensive variables, at constant total volume, thereby altering also the conjugate variables, i.e. the intensive properties, which closes the irreversible loop. This cycle can also be initiated by starting with a zero piston speed but non-zero driving forces for phase change. In that way, the irreversible loop is initiated, and through the changing multiphase pressure also the piston is finally put in motion.

5. Conclusions and discussion

Crystallization of a two-phase system enclosed in a piston has been studied by means of three thermodynamic formalisms, namely, Lui's procedure of rational nonequilibrium thermodynamics, the Matrix Model, and the GENERIC formalism. These methods differ substantially in structure, e.g. reversible-irreversible splitting, degeneracy

requirements, open versus closed systems. Concerning the last difference, the Matrix Model discussed the dynamics for Eqs. (4b) and (4h) under isothermal conditions and for externally-controlled piston speed, whereas rational thermodynamics as well as GENERIC include thermal effects and the dynamics of the piston, i.e. they describe the entire system (4a-4h) with an additional thermal variable with the corresponding Eq. (15) and (23), respectively. It was discussed that the two-generator nature of the GENERIC formalism allowed for a flexible choice of the thermal variable due to the degeneracy requirements, which ensure that the full thermodynamic information is finally contained in the dynamic equations.

All three methods found the same expression for the multiphase pressure on the piston, \bar{p} , given by (17) and (21). All three methods also agreed in that the phase change happens at constant volume, at least instantaneously. As far as the phase change dynamics is concerned, the difference between rational thermodynamics on the one hand and the Matrix Model and GENERIC on the other hand became apparent. In short, the rational thermodynamics treatment constrains only those phase change contributions that appear in the entropy production rate, whereas the other two methods allow to make a statement about all phase change contributions. The results are not in contradiction, but merely show the consequences of implementing the dissipation inequality differently. While the latter is a single inequality and enters as such into the rational thermodynamics treatment, the Matrix Model and GENERIC formalisms impose substantially more conditions in terms of the positivity of a matrix and its Onsager–Casimir symmetry. The consequences of these supplementary constraints have surfaced clearly in the discussion of the phase change dynamics. This constitutes a major result of this study. The detailed discussion of phase change contributions in the dynamic equations in Section 4.5 has also revealed where physical effects such as impingement of crystallites, depletion zones, and crystal shape recognition are to be incorporated in a thermodynamically consistent manner.

Fig. 2, discussed previously, serves as a summary of the coupling and the sequence of events as described by the dynamic equations. In particular one notices that, e.g. for given compression due to the piston, the system is not directly driven into the phase with higher density. It is rather an indirect effect via a change in morphology, followed by a change in intensive variables such as pressures and chemical potentials, which in their turn then alter the thermodynamic driving force for phase change. Roughly speaking, increasing pressure in the system changes the volume contribution Π_V to the driving forces (43) in such a way that it favors the phase with lower specific volume, i.e. higher density. This shows that the dynamic model for phase transition developed here follows the same basic concepts as expected from equilibrium thermodynamic thinking, but additionally provides the latter with the dynamic picture, including morphological details about the intermediate stages between the

equilibrium states. It is obvious that the thermodynamic description of a specific system of interest, e.g. carbon and water as discussed in the introduction, most prominently enter in the reversible loop in Fig. 2, where the changes in morphological variables needs to be translated into changes in the intensive variables.

Finally, we would like to comment on the force-flux relationship for phase change, (39). It is a well-known problem in irreversible thermodynamics to identify the basic dissipative processes in a physically meaningful way. For the specific system studied here, a natural choice for the fluxes seems to be the phase change contributions to the morphological variables, which is the strategy followed above. This led to a 4×4 -matrix \mathbf{R} , which relates the forces and fluxes. However, this matrix has only rank two since it describes two phenomena, namely nucleation and growth. One might wonder whether rewriting the matrix in the form $\mathbf{R} = \mathbf{Q}^T \cdot \mathbf{R}' \cdot \mathbf{Q}$, where \mathbf{R}' is a 2×2 -, and \mathbf{Q} a 2×4 -matrix, results in a physically more meaningful interpretation of forces and fluxes. In particular, one would then have only two forces and only two fluxes, corresponding to nucleation and volumetric growth. However, such a route will not be taken since it would distract from the fact that, for a general system, the growth rates as appearing in the Schneider rate equations do not necessarily have to be equal. They rather offer means to implement more detailed physics as far as morphology formation is concerned.

Acknowledgements

The author is grateful to Professor R.J.J. Jongschaap, Professor W. Muschik, and Professor H.C. Öttinger for useful discussions. Financial support from the Swiss National Science Foundation under grant no. 81EZ-68591 is gratefully acknowledged.

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