Thermodynamically consistent incorporation of the Schneider rate equations into two-phase models

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We formulate a solid-liquid two-phase model including viscous stresses, heat conduction in the two phases, as well as heat exchange through the interface, and a phase change in the structure of nonequilibrium thermodynamics described by a general equation for the nonequilibrium reversible-irreversible coupling (GENERIC). The evolution of the microstructure is studied in terms of the Schneider rate equations introducing the nucleation rate and the radial growth rate of the solid phase. The application of the GENERIC structure shows that this radial growth factor is not an additional, independent material function but is to be expressed in terms of the difference in the chemical potentials, in the temperatures, and in the pressures between the two phases. The contribution due to the pressure difference appears in conjunction with the surface tension in such a way, that a driving force results only if deviations from a generalized version of the Laplace equation occur. Furthermore, it is found that for conditions under which the radial growth rate is zero, the nucleation rate must vanish.

I. INTRODUCTION

It is well accepted that the phase diagram of a material can be determined (in principle) from a given thermodynamic potential. The use of equilibrium thermodynamics, in this context in particular the extremum criteria (and the criteria and constructions derived thereof), has shown to be of invaluable help. However, only little is known about the *dynamics* of the phase change and about its governing equations and criteria. This paper attempts to show how nonequilibrium formalisms can be used as a guideline to close this considerable gap. For this purpose, we unite a continuum two-phase model [1] with the Schneider rate equations [2], the latter giving a coarse-grained picture of the structural changes during phase transformation, in the framework of general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) [3,4]. This paper is organized as follows. First, a brief overview over the two-phase model and over the Schneider rate equations is given, before the essentials of the GENERIC formalism are outlined. Then, a model that unifies two-phase flow and the Schneider rate equations is incrementally developed using GENERIC as a guideline.

A. Two-phase flow

The description of two-phase flow adopted here consists of the hydrodynamic variables for both of the two phases, and in addition, of the volume fraction of one phase and of the amount of interface per unit volume. Hence, the microstructure is characterized on a rather coarse level, having the

advantage that such a model is suitable for finite element simulations. A comprehensive introduction to this type of two-phase flow model can be found in the books of Ishii [1] and Drew and Passman [5]. In the following, we consider the case of equal velocities of the two phases, thereby reducing the set of variables and of equations. This approximation is justified either by neglecting external forces and relative diffusion of the two phases or by assuming infinitely high interfacial friction between the two phases [1,6]. We may hence choose the following fields as independent variables for the solid(s)-liquid(l) two-phase system: the apparent mass densities $\rho_\alpha(\mathbf{r})$ ($\alpha = s,l$), and the apparent internal energy densities $\epsilon_\alpha(\mathbf{r})$ ($\alpha = s,l$) where all apparent densities are the intrinsic densities per unit volume of the constituent times the volume fraction of the respective constituent, the total momentum density $\mathbf{u}(\mathbf{r})$ of the two phases, as well as the volume fraction of solid $\phi(\mathbf{r})$ and the amount of interface per unit volume $\psi(\mathbf{r})$. The velocity field $\mathbf{v}(\mathbf{r})$ is given by $\mathbf{u}(\mathbf{r}) = [\rho_s(\mathbf{r}) + \rho_l(\mathbf{r})]\mathbf{v}(\mathbf{r})$. Since we intend to also include the Schneider rate equations into the model and hence can follow the time evolution of the volume fraction, the mass transfer during phase change can be related to the change in volume fraction (in contrast to the linear constitutive equation on p.172 in Ref. [1]). If the rate of change of the volume fraction ϕ due to phase change is denoted by $\dot{\phi}|_{\text{pc}}$, the rate of mass transfer is proportional to the phase change rate, $\hat{\rho}\dot{\phi}|_{\text{pc}}$. The governing equations then read when neglecting turbulent contributions [1]

$$\partial_t \rho_s + \nabla \cdot (\mathbf{v}\rho_s) = +\hat{\rho}\dot{\phi}|_{\text{pc}}, \quad (1)$$

$$\partial_t \rho_l + \nabla \cdot (\mathbf{v}\rho_l) = -\hat{\rho}\dot{\phi}|_{\text{pc}}, \quad (2)$$

$$\partial_t \mathbf{u} + \nabla \cdot (\mathbf{v}\mathbf{u}) = -\nabla(p_s + p_l) + \nabla \cdot (\boldsymbol{\tau}_s + \boldsymbol{\tau}_l) + \mathbf{u}^\sigma, \quad (3)$$

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$$\partial_t \epsilon_s + \nabla \cdot (\mathbf{v}\epsilon_s) = -p_s(\nabla \cdot \mathbf{v}) + \boldsymbol{\tau}_s : (\nabla \mathbf{v}) - \nabla \cdot \mathbf{q}_s + \epsilon_s^q$$
$$+ \epsilon_s^\Gamma \dot{\phi}|_{pc}, \tag{4}$$

$$\partial_t \epsilon_l + \nabla \cdot (\mathbf{v}\epsilon_l) = -p_l(\nabla \cdot \mathbf{v}) + \boldsymbol{\tau}_l : (\nabla \mathbf{v}) - \nabla \cdot \mathbf{q}_l + \epsilon_l^q - \epsilon_l^\Gamma \dot{\phi}|_{pc}. \tag{5}$$

Let us briefly comment on the various contributions (for more details the reader is referred to Refs. [1,6]).

Using $\phi_s \equiv \phi$ and $\phi_l \equiv 1 - \phi$, the pressures p_α are given by $p_\alpha = \phi_\alpha \tilde{p}_\alpha$, $\tilde{p}_\alpha$ denoting the pressure in phase α, and the viscous stresses and heat fluxes are expressed as

$$\boldsymbol{\tau}_\alpha = \phi_\alpha \eta_\alpha [(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T] + 2\phi_\alpha \hat{\kappa}_\alpha (\nabla \cdot \mathbf{v})\mathbf{1}, \tag{6}$$

$$\mathbf{q}_\alpha = -\phi_\alpha \boldsymbol{\lambda}_\alpha \cdot (\nabla T_\alpha), \tag{7}$$

with the effective viscosities η_α, the effective dilational viscosities κ_α, $\hat{\kappa}_\alpha = \kappa_\alpha/2 - \eta_\alpha/3$, and the (generally anisotropic) effective heat conduction tensors $\boldsymbol{\lambda}_\alpha$ (for details, see Ref. [6]). The last term in Eq. (6) is absent in Refs. [1,6] but in analogy to classical, one-phase hydrodynamics one might wish to include it. The reader should notice that in the context of the two-phase models discussed here, all these phenomenological coefficients also depend on the microstructure, i.e., on ϕ and ψ [1,6]. A detailed discussion of the different phenomena included in the effective viscosity η_α is given, e.g., in Ref. [7]. In particular, the constitutive assumption (6) also holds for the rigid solid phase as long as the crystallites do not merge to form a single big crystal [6,7]. This peculiarity originates from the fact that the spatial resolution of the model presented here is larger than the size of the individual crystallites.

In the momentum balance Eq. (3), the term $\mathbf{u}^\sigma$ denotes the effect of the surface tension σ given by (see, e.g., Refs. [1,6])

$$\mathbf{u}^\sigma = \nabla(\phi H \sigma), \tag{8}$$

where the coarse-grained mean curvature H depends on the microstructure, $H(\phi, \psi)$. It is noteworthy that the interfacial momentum source (8) is such that it modifies the bulk pressure contribution in Eq. (3). Another effect of the interface is the possibility to exchange heat through the contact interface, hence there is a heat-flow proportional to the interfacial area. If $\lambda_\alpha^{(0)}$ denotes the microscopic heat conductivity, $l_\alpha^{(0)}$ is a characteristic microscopic heat conduction length, and T_i stands for the temperature of the interface, the interfacial energy change in phase α due to interfacial heat transfer is given by Refs. [1,6]

$$\epsilon_\alpha^q = \psi \frac{\lambda_\alpha^{(0)}}{l_\alpha^{(0)}} (T_i - T_\alpha). \tag{9}$$

The rate of phase change affects not only the mass balances (1),(2) as discussed above, but also the internal energy balances (4),(5). The corresponding contributions are determined by [1,6]

$$\epsilon_\alpha^\Gamma = \hat{\rho} \bar{h}_{\alpha i} - \tilde{p}_{\alpha i}, \tag{10}$$

where $\bar{h}_{\alpha i}$ denotes the enthalpy per unit mass of phase α, and $\tilde{p}_{\alpha i}$ is the pressure of phase α at the interface. Since the volume element, which defines the resolution of our model, is larger than the microstructures, it is necessary to introduce two different pressures, namely the bulk pressure $\tilde{p}_\alpha$ and the interface pressure $\tilde{p}_{\alpha i}$ in order not to lose too much detail. In general, the interfacial pressures are a subtle issue and have to be discussed for the specific problem at hand. For example, in liquid-solid two-phase systems one might assume $\tilde{p}_{li} = \tilde{p}_l$ due to relatively fast pressure equilibration in the liquid phase. As far as the solid phase is concerned, it is claimed in some references [6–8] that, as long as the solid ''crystals'' are completely surrounded by liquid and there are no contacts between crystals, one has $\tilde{p}_{si} = \tilde{p}_s$. However, if there is significant contact between the crystals or if the solid forms a continuous structure, additional pressure contributions occur in the solid [6–8]. It is commonly assumed that the difference of the interfacial pressures relates to the mean curvature H of the interface and to the surface tension σ through $\tilde{p}_{si} - \tilde{p}_{li} = \sigma H$ on which (8) is based. In the following, fast pressure equilibration in the liquid phase and no contact between solid particles is assumed, i.e., $\tilde{p}_{\alpha i} = \tilde{p}_\alpha$. Similar to the pressures, one also needs to distinguish between the bulk enthalpies $\bar{h}_\alpha$ and the interfacial enthalpies $\bar{h}_{\alpha i}$. It is well established that the difference between the interfacial enthalpies (and not the difference between their bulk counterparts) equals the latent heat $L = \bar{h}_{li} - \bar{h}_{si}$. A discussion of possible closures for the interfacial enthalpies $\bar{h}_{\alpha i}$ can be found in Refs. [1,6].

It is evident that the above set of Eqs. (1)–(5) is not closed for two reasons. First, in the above equations, the temperature of the interface enters, both directly trough ϵ_α^q given in Eq. (9), as well as implicitly through $\sigma(T_i)$. Since it is desirable to have the interfacial temperature as a dynamical variable rather than as a constant, a corresponding equation is required. In Ref. [1], such an equation is presented if some approximations can be made. It will be shown in Sec. II that the equation describing the dynamics of T_i (or of an equivalent variable) naturally arises when using the GENERIC formalism. Second, the above set of Eqs. (1)–(5) is not closed because there are no evolution equations for the microstructural variables ϕ and ψ. In order to close the system of equations, we here consider the Schneider rate equations.

B. Schneider rate equations

In 1939–1941, Avrami studied the kinetics of phase change and developed the well-known Avrami equation [9]

to follow the time evolution of the volume fraction ϕ of the solid phase. Since this equation is an integral equation depending on the whole history of the process and is hence complicated to solve, Schneider, Köppel, and Berger [2] transformed the integral equation into a set of four coupled differential equations for the variables $\{\Psi_0, \Psi_1, \Psi_2, \Psi_3\}$ under quiescent conditions, where the physical volume fraction ϕ and the amount of interface per unit volume ψ can be expressed in terms of $\{\Psi_0, \Psi_1, \Psi_2, \Psi_3\}$. When accommodating the original Schneider equations to flow conditions, the convection mechanism for the variables $\{\Psi_0, \Psi_1, \Psi_2, \Psi_3\}$ needs special care. The explicit form of the convection shall be addressed when formulating the model in the GENERIC framework. In the following, the dynamics of the structural variables is split into a convective and a phase change contribution, which are hereafter denoted by the subscripts ''conv'' and ''pc,'' respectively,

$$\partial_t \Psi_0 = \dot{\Psi}_0|_{\text{conv}} + \dot{\Psi}_0|_{\text{pc}}, \quad \dot{\Psi}_0|_{\text{pc}} := G(T)\Psi_1, \quad (11)$$

$$\partial_t \Psi_1 = \dot{\Psi}_1|_{\text{conv}} + \dot{\Psi}_1|_{\text{pc}}, \quad \dot{\Psi}_1|_{\text{pc}} := G(T)\Psi_2, \quad (12)$$

$$\partial_t \Psi_2 = \dot{\Psi}_2|_{\text{conv}} + \dot{\Psi}_2|_{\text{pc}}, \quad \dot{\Psi}_2|_{\text{pc}} := G(T)\Psi_3, \quad (13)$$

$$\partial_t \Psi_3 = \dot{\Psi}_3|_{\text{conv}} + \dot{\Psi}_3|_{\text{pc}}, \quad \dot{\Psi}_3|_{\text{pc}} := 8\pi\alpha(T), \quad (14)$$

describing the growth of spherulitic structures, where $G(T)$ (in units of m s^{-1}) is a radial growth rate, and $\alpha(T)$ [m^{-3} s^{-1}] denotes the nucleation rate. The variables $\{\Psi_0, \Psi_1, \Psi_2, \Psi_3\}$ disregard the fact that, first, nuclei can be swallowed by other growing crystallites, and, second, that different crystallites may impinge as crystallization proceeds. Hence, the above quantities are called ''unrestricted.'' Ψ_0 denotes the unrestricted volume fraction, Ψ_1 is the unrestricted surface per unit volume, Ψ_2 is the total length of the crystallites per unit volume, and Ψ_3 represents the number of nuclei per unit volume. As in the two-phase model, the restricted (physical) volume fraction and interfacial area instead of their unrestricted counterparts occur, it is essential to relate the two descriptions. There are two common relations between the real (i.e., restricted) and the unrestricted volume fraction of the form $\phi = \phi(\Psi_0)$ [with $d\phi/d\Psi_0 > 0$, $\phi(\Psi_0 = 0) = 0$, and $\lim_{\Psi_0 \to \infty} \psi(\Psi_0) = 1$], namely,

$$\phi := 1 - e^{-\Psi_0}, \quad \text{i.e.,} \quad \Psi_0 = -\ln(1 - \phi) \text{ Avrami [9]},$$
$$(15)$$

$$\phi := \frac{\Psi_0}{1 + \Psi_0}, \quad \text{i.e.,} \quad \Psi_0 = \frac{\phi}{1 - \phi} \text{ Tobin [10].} \quad (16)$$

The coupled Schneider rate equations can be mapped from the set $\{\Psi_0, \Psi_1, \Psi_2, \Psi_3\}$ onto $\{\phi, \psi, \Psi_2, \Psi_3\}$:

$$\partial_t \phi = \dot{\phi}|_{\text{conv}} + \dot{\phi}|_{\text{pc}}, \quad \dot{\phi}|_{\text{pc}} := G(T)\psi, \quad (17)$$

$$\partial_t \psi = \dot{\psi}|_{\text{conv}} + \dot{\psi}|_{\text{pc}}, \quad \dot{\psi}|_{\text{pc}} := G(T)\mathcal{L}(\phi, \psi, \Psi_2), \quad (18)$$

$$\partial_t \Psi_2 = \dot{\Psi}_2|_{\text{conv}} + \dot{\Psi}_2|_{\text{pc}}, \quad \dot{\Psi}_2|_{\text{pc}} = G(T)\Psi_3, \quad (19)$$

$$\partial_t \Psi_3 = \dot{\Psi}_3|_{\text{conv}} + \dot{\Psi}_3|_{\text{pc}}, \quad \dot{\Psi}_3|_{\text{pc}} = 8\pi\alpha(T), \quad (20)$$

where

$$\psi := \left(\frac{d\Psi_0}{d\phi}\right)^{-1} \Psi_1, \quad (21)$$

$$\mathcal{L}(\phi, \psi, \Psi_2) = \left(\frac{d\Psi_0}{d\phi}\right)^{-1} \left(\Psi_2 - \frac{d^2\Psi_0}{d\phi^2}\psi^2\right). \quad (22)$$

The Schneider rate equations (11)–(14) as given above have been used by Eder and Janeschitz-Kriegl to study the crystallization of quiescent polymer melts [11–15]. Furthermore, since the Schneider equations allow us to modify the phase change kinetics at different levels, it has even been possible to capture a number of essential phenomena occurring in the crystallization of sheared polymer melts [14,15]. In their work, the (modified) Schneider rate equations are solved simultaneously with a temperature equation including latent heat effects. In the procedure presented here this temperature equation is replaced by the internal energy balances and hence arises as a dependent equation. The above-mentioned applications of the Schneider rate equations clearly demonstrate their practical use and the strong need to relate them to a nonequilibrium context.

C. GENERIC structure

Recently, a general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) has been developed for describing nonequilibrium systems [3,4]. When trying to formulate a model in the GENERIC framework, the first step is to choose the variables that describe the system. Similar to the procedure in equilibrium thermodynamics, the choice of variables must be such that they are independent and sufficient to capture the essential physics. Such a set of variables shall here be denoted by x. Note that x may have both discrete indices as well as continuous indices (for field variables). According to GENERIC, the time evolution of the variables x can be written in the form

$$\frac{dx}{dt} = L(x)\frac{\delta E}{\delta x} + M(x)\frac{\delta S}{\delta x}, \quad (23)$$

where the two generators E and S are the total energy and entropy functionals in terms of the state variables x and L and M are certain matrices (operators). The matrix multiplications imply not only summations over discrete indices but may also include integration over continuous variables, and $\delta/\delta x$ typically implies functional rather than partial derivatives (for more details see [3,4]). The GENERIC structure

also imposes certain conditions on the building blocks in Eq. (23). First, Eq. (23) is supplemented by the degeneracy requirements

$$L(x)\frac{\delta S}{\delta x}=0, \qquad (24)$$

$$M(x)\frac{\delta E}{\delta x}=0. \qquad (25)$$

The requirement that the (functional) derivative of the entropy lies in the null space of L represents the reversible nature of L. Hence, the functional form of S and L are constrained such that the entropy is not affected by the operator generating the reversible dynamics, i.e., by L. On the other hand, the requirement that the functional derivative 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 antisymmetric and fulfill the Jacobi identity, whereas M needs to be positive semidefinite and Onsager-Casimir symmetric. As a result of all these conditions one may easily show that the GENERIC Eq. (23) 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 Eq. (23) are called the reversible and irreversible contributions, respectively.

Both the complementary degeneracy requirements and the symmetry properties are essential for formulating proper L and M matrices when modeling concrete nonequilibrium problems. The list of systems, which have already been expressed in the GENERIC form includes classical hydrodynamics, polymer kinetic theory (including hydrodynamic interaction, rigid constraints, reptation models, and polymer heat conductivity), chemical reactions, Boltzmann's kinetic equation, and the Doi-Ohta model. These various applications have shown that the two-generator idea and the degeneracy requirements have strong implications. In order to justify this approach, these elements of GENERIC, originally discovered by empirical observations, have been derived by projection operator formalisms [16,17], which strongly encourages us to use the GENERIC formalism.

II. GENERIC FORMULATION OF A TWO-PHASE MODEL

We here unify the two-phase model given by Eqs. (1)–(5) with the Schneider rate Eqs. (17)–(20) in the GENERIC framework, thereby also constructing the appropriate equations for the thermodynamic variables of the interface.

A. Set of variables and generating functionals

The solid(s)-liquid(l) two-phase system is described in terms of the following variables. First, the two phases are characterized by the apparent mass densities $\rho_\alpha(\mathbf{r})$ ($\alpha=s,l$), and the apparent internal energy densities $\epsilon_\alpha(\mathbf{r})$ ($\alpha=s,l$) where all four apparent densities denote the intrinsic densities per unit volume of the constituent times the volume fraction of the respective constituent. Second, the corresponding

quantities for the interface are the apparent interfacial mass density, $\rho_i(\mathbf{r})$, and the apparent internal energy density, $\epsilon_i(\mathbf{r})$. As previously discussed, it is sufficient under the equal velocity assumption to describe the flow by only one momentum density, where in the following the total momentum density $\mathbf{u}(\mathbf{r})$ accounts for both the momentum of the two phases as well as for the momentum of the interface, in contrast to Sec. I A. And finally, according to the reformulated Schneider rate Eqs. (17)–(20), the microstructure shall be described by the volume fraction ϕ, the interfacial area ψ per unit volume, by the unrestricted length Ψ_2 per unit volume, and by the unrestricted number of crystallites Ψ_3 per unit volume. The set of variables $\mathbf{x}$ to describe the system is therefore

$$\mathbf{x}=\{\rho_s,\rho_l,\rho_i,\mathbf{u},\epsilon_s,\epsilon_l,\epsilon_i,\phi,\psi,\Psi_2,\Psi_3\}. \qquad (26)$$

Natural expressions for the energy functional E and for the entropy functional S are obtained by the local equilibrium assumption. If the thermodynamics of the solid and of the liquid phase is characterized by the two branches s_s and s_l of the entropy density and the thermodynamics of the interface is given by the entropy density s_i, the generating functionals E and S read

$$E[\mathbf{x}]=\int\left(\frac{1}{2}\frac{\mathbf{u}^2}{\rho_s+\rho_l+\rho_i}+\epsilon_s+\epsilon_l+\epsilon_i\right)d^3r, \qquad (27)$$

$$S[\mathbf{x}]=\int[\phi s_s(\tilde{\rho}_s,\tilde{\epsilon}_s)+(1-\phi)s_l(\tilde{\rho}_l,\tilde{\epsilon}_l)+\psi s_i(\tilde{\rho}_i,\tilde{\epsilon}_i)]d^3r \qquad (28)$$

where the intrinsic quantities denoted by ''$\sim$'' for the indices (s,l) are densities per volume of the respective phase (and not with respect to the total volume of the volume element) and for the index i are densities per amount of interface per unit volume. They can be expressed in terms of the corresponding apparent variables contained in $\mathbf{x}$ as

$$\tilde{\rho}_s=\tilde{\rho}_s(\rho_s,\phi)=\frac{\rho_s}{\phi}, \qquad (29)$$

$$\tilde{\rho}_l=\tilde{\rho}_l(\rho_l,\phi)=\frac{\rho_l}{1-\phi}, \qquad (30)$$

$$\tilde{\rho}_i=\tilde{\rho}_i(\rho_i,\psi)=\frac{\rho_i}{\psi}, \qquad (31)$$

$$\tilde{\epsilon}_s=\tilde{\epsilon}_s(\epsilon_s,\phi)=\frac{\epsilon_s}{\phi}, \qquad (32)$$

$$\tilde{\epsilon}_l=\tilde{\epsilon}_l(\epsilon_l,\phi)=\frac{\epsilon_l}{1-\phi}, \qquad (33)$$

$$\tilde{\epsilon}_i=\tilde{\epsilon}_i(\epsilon_i,\psi)=\frac{\epsilon_i}{\psi}. \qquad (34)$$

The following assumptions are implied in the above expressions for the energy and entropy functionals. The current model includes neither the configurational entropy of the interface nor accounts for the relative arrangement of the crystallites. Disregarding the latter is in agreement with neglecting the relative diffusion of the two phases as discussed in Sec. I A. Furthermore, the pressure due to collisions between crystallites is not captured in the model presented here. In accordance with the comments on the interfacial pressures in Sec. I A, the current GENERIC model hence represents the situation $\tilde{p}_{si} = \tilde{p}_s$ (and $\tilde{p}_{li} = \tilde{p}_l$). Using the following definitions for the temperatures, the chemical potentials per unit mass, and the pressures of the two phases and of the interface (i.e., for $\alpha = s, l, i$),

$$T_\alpha(\mathbf{r}) = \left(\frac{\partial s_\alpha(\tilde{\rho}_\alpha, \tilde{\epsilon}_\alpha)}{\partial \tilde{\epsilon}_\alpha} \right)^{-1}, \tag{35}$$

$$\frac{\mu_\alpha(\mathbf{r})}{T_\alpha(\mathbf{r})} = - \frac{\partial s_\alpha(\tilde{\rho}_\alpha, \tilde{\epsilon}_\alpha)}{\partial \tilde{\rho}_\alpha}, \tag{36}$$

$$\frac{\tilde{p}_\alpha(\mathbf{r})}{T_\alpha(\mathbf{r})} = s_\alpha(\tilde{\rho}_\alpha, \tilde{\epsilon}_\alpha) - \tilde{\epsilon}_\alpha \frac{\partial s_\alpha(\tilde{\rho}_\alpha, \tilde{\epsilon}_\alpha)}{\partial \tilde{\epsilon}_\alpha} - \tilde{\rho}_\alpha \frac{\partial s_\alpha(\tilde{\rho}_\alpha, \tilde{\epsilon}_\alpha)}{\partial \tilde{\rho}_\alpha}, \tag{37}$$

one finds for the functional derivatives of E and S

$$\frac{\delta E}{\delta \mathbf{x}} = \begin{pmatrix} -\frac{1}{2}\mathbf{v}^2 \\ -\frac{1}{2}\mathbf{v}^2 \\ -\frac{1}{2}\mathbf{v}^2 \\ \mathbf{v} \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \frac{\delta S}{\delta \mathbf{x}} = \begin{pmatrix} -\frac{\mu_s}{T_s} \\ -\frac{\mu_l}{T_l} \\ -\frac{\mu_i}{T_i} \\ 0 \\ \frac{1}{T_s} \\ \frac{1}{T_l} \\ \frac{1}{T_i} \\ \frac{\tilde{p}_s}{T_s} - \frac{\tilde{p}_l}{T_l} \\ \frac{\tilde{p}_i}{T_i} \\ 0 \\ 0 \end{pmatrix}, \tag{38}$$

where the velocity field $\mathbf{v}(\mathbf{r})$ is given by $\mathbf{u}(\mathbf{r}) = [\rho_s(\mathbf{r}) + \rho_l(\mathbf{r}) + \rho_i(\mathbf{r})]\mathbf{v}(\mathbf{r})$.

B. Reversible dynamics

In order to determine the reversible dynamics, we now construct the operator $\mathbf{L}$. It has been discussed and illustrated in Ref. [4] that this operator is closely related to the generator of space transformations on the field variables (scalars, scalar densities, and vector densities). As an extension of classical one-phasic hydrodynamics [4], we propose the following form for the operator $\mathbf{L}$

$$\mathbf{L}(\mathbf{r}) = \begin{pmatrix} 0 & 0 & 0 & \mathbf{L}_{\rho_s \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\rho_l \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\rho_i \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \mathbf{L}_{\mathbf{u}\rho_s} & \mathbf{L}_{\mathbf{u}\rho_l} & \mathbf{L}_{\mathbf{u}\rho_i} & \mathbf{L}_{\mathbf{uu}} & \mathbf{L}_{\mathbf{u}\epsilon_s} & \mathbf{L}_{\mathbf{u}\epsilon_l} & \mathbf{L}_{\mathbf{u}\epsilon_i} & \mathbf{L}_{\mathbf{u}\phi} & \mathbf{L}_{\mathbf{u}\psi} & \mathbf{L}_{\mathbf{u}\Psi_2} & \mathbf{L}_{\mathbf{u}\Psi_3} \\ 0 & 0 & 0 & \mathbf{L}_{\epsilon_s \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\epsilon_l \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\epsilon_i \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\phi \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\psi \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\Psi_2 \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{L}_{\Psi_3 \mathbf{u}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \tag{39}$$

with

$$\mathbf{L}_{\rho_s \mathbf{u}} = -\nabla \rho_s \qquad \mathbf{L}_{\mathbf{u}\rho_s} = -\rho_s \nabla, \qquad (40a)$$

$$\mathbf{L}_{\rho_l \mathbf{u}} = -\nabla \rho_l \qquad \mathbf{L}_{\mathbf{u}\rho_l} = -\rho_l \nabla, \qquad (40b)$$

$$\mathbf{L}_{\rho_i \mathbf{u}} = -\nabla \rho_i \qquad \mathbf{L}_{\mathbf{u}\rho_i} = -\rho_i \nabla, \qquad (40c)$$

$$\mathbf{L}_{\mathbf{uu}} = -[\nabla \mathbf{u} + \mathbf{u}\nabla]^T, \qquad (40d)$$

$$\mathbf{L}_{\epsilon_s \mathbf{u}} = -\nabla \epsilon_s - p_s \nabla \qquad \mathbf{L}_{\mathbf{u}\epsilon_s} = -\epsilon_s \nabla - \nabla p_s, \qquad (40e)$$

$$\mathbf{L}_{\epsilon_l \mathbf{u}} = -\nabla \epsilon_l - p_l \nabla \qquad \mathbf{L}_{\mathbf{u}\epsilon_l} = -\epsilon_l \nabla - \nabla p_l, \qquad (40f)$$

$$\mathbf{L}_{\epsilon_i \mathbf{u}} = -\nabla \epsilon_i - \tfrac{2}{3} p_i \nabla \qquad \mathbf{L}_{\mathbf{u}\epsilon_i} = -\epsilon_i \nabla - \tfrac{2}{3}\nabla p_i, \qquad (40g)$$

$$\mathbf{L}_{\phi \mathbf{u}} = -\nabla \phi + \phi \nabla \qquad \mathbf{L}_{\mathbf{u}\phi} = -\phi \nabla + \nabla \phi, \qquad (40h)$$

$$\mathbf{L}_{\psi \mathbf{u}} = -\nabla \psi + \tfrac{2}{3}\psi \nabla \qquad \mathbf{L}_{\mathbf{u}\psi} = -\psi \nabla + \tfrac{2}{3}\nabla \psi, \qquad (40i)$$

$$\mathbf{L}_{\Psi_2 \mathbf{u}} = -\nabla \Psi_2 + \tfrac{1}{3}\Psi_2 \nabla \qquad \mathbf{L}_{\mathbf{u}\Psi_2} = -\Psi_2 \nabla + \tfrac{1}{3}\nabla \Psi_2, \qquad (40j)$$

$$\mathbf{L}_{\Psi_3 \mathbf{u}} = -\nabla \Psi_3 \qquad \mathbf{L}_{\mathbf{u}\Psi_3} = -\Psi_3 \nabla, \qquad (40k)$$

and with the apparent pressures $p_s = \phi \tilde{p}_s$, $p_l = (1-\phi)\tilde{p}_l$, and $p_i = \psi \tilde{p}_i$. The derivatives act on all terms to the right of them. The matrix $\mathbf{L}$ given by Eqs. (39), (40) is antisymmetric and satisfies the Jacobi identity. Furthermore, the degeneracy (24) is fulfilled due to the expressions for the pressures (37). The elements $\mathbf{L}_{\rho_i,\mathbf{u}}$ and $\mathbf{L}_{\epsilon_i,\mathbf{u}}$, giving rise to the reversible dynamics of the mass density (in accordance with Refs. [18,19]) and the internal energy density of the interface [which are absent in Eqs. (1)–(5)] are justified on one hand by analogy with the variables ρ_s and ρ_l and ϵ_s and ϵ_l, respectively, and on the other hand by the compatibility with the GENERIC antisymmetry and degeneracy requirements on $\mathbf{L}$. It can be shown easily that $\mathbf{L}(\mathbf{r}) \cdot \delta E / \delta \mathbf{x}(\mathbf{r})$ gives rise to all reversible contributions in Eqs. (1)–(5) and (17)–(20), i.e., to the convection mechanisms and the pressure contributions including a momentum source due to the pressure of the interface. If the surface tension σ is defined in terms of the pressure of the interface $\tilde{p}_i$ by $\sigma = -\tilde{p}_i$, one obtains for the momentum source term $\mathbf{u}^\sigma = -\tfrac{2}{3}\nabla p_i = \nabla(\tfrac{2}{3}\psi \sigma)$ rather than $\mathbf{u}^\sigma = \nabla(\phi H \sigma)$ as given by Eq. (8) where the curvature H is involved. This discrepancy originates from the fact that in the generating functionals E and S only the area of the interface enters, thereby not accounting for curvature. However, for the specific case of spherical particles, the GENERIC expression for $\mathbf{u}^\sigma$ coincides with Eq. (8) since $H(\phi,\psi) = \tfrac{2}{3}\psi/\phi$ (see, e.g., p.178 in Ref. [1]). A further difference between Eqs. (1)–(5) and the GENERIC formulation presented here is that the latter accounts for a mass density of the interface that is absent in Eqs. (1)–(5), explaining why the momentum density as used in Eq. (27) includes also an interface contribution in contrast to the momentum density used in Eq. (3).

Let us finally comment on the convection of the structural variables, i.e., on the form of the elements $\mathbf{L}_{\phi\mathbf{u}}$, $\mathbf{L}_{\psi\mathbf{u}}$, $\mathbf{L}_{\Psi_2\mathbf{u}}$, and $\mathbf{L}_{\Psi_3\mathbf{u}}$. The fact that all four structural variables have a different convection mechanism is motivated by the following argument. Considering the change in the structural variables when simply blowing up the volume element isotropically, it is easily seen that the volume fraction does not change, while the other quantities change since the surface area, the length, and the number scale differently than the volume element under blowing up. This analysis explains why the volume fraction ϕ is convected as a scalar in accordance with literature (see, e.g., Refs. [18–21]), whereas the number density Ψ_3 is naturally convected as a scalar density. The ''intermediate'' variables ψ and Ψ_2 accordingly are found to transform as indicated in the corresponding expressions in Eq. (40). It should be mentioned that the amount of interface per unit volume ψ is sometimes proposed to be convected as a scalar density (see, e.g., [1,8,22]) whereas the convection mechanism proposed above is in agreement with Ref. [23]. Furthermore, as the Doi-Ohta model for multiphase flow shows, the shape of the interface enters the convection of ψ [23,24]. However, since such detail is not included in the current description, the element $\mathbf{L}_{\psi\mathbf{u}}$ gives a fair description of the convection of ψ.

C. Irreversible dynamics

In this section, we construct the matrix $\mathbf{M}$ representing the irreversible effects in Eqs. (1)–(5) and (17)–(20), i.e., viscous stresses, heat conduction in the bulk of the two phases, and through the interface, and phase change. Due to the different origin of the effects, $\mathbf{M}$ will be a sum of different contributions, each representing one specific phenomenon, i.e.,

$$\mathbf{M}(\mathbf{r}) = \mathbf{M}^\eta(\mathbf{r}) + \mathbf{M}^\lambda(\mathbf{r}) + \mathbf{M}^q(\mathbf{r}) + \mathbf{M}^{\mathrm{pc}}(\mathbf{r}), \qquad (41)$$

corresponding to viscous stresses, heat flow in the two phases, heat transport across the interface, and phase change, respectively. The criteria of GENERIC imposed on $\mathbf{M}$ are such that they can be verified for each contribution individually in order to guarantee the compatibility with GENERIC of the total dissipative dynamics. Hence, in the following, we will show that each of the contributions is Onsager-Casimir symmetric, is positive-semidefinite and fulfills the degeneracy requirement (25).

Before we proceed to the detailed discussion of the irreversible contributions, we here briefly mention the general guideline along which the corresponding matrices $\mathbf{M}$ are constructed. First, one lists the variables that are involved. It may either be that the effect under consideration makes a contribution in the balance equation of these variables, or that the functional derivatives of the entropy with respect to these variables may help to construct meaningful driving forces for the effect under consideration. Then, all other elements in $\mathbf{M}$ that are not related to any of these variables should be set to zero. In order to simplify the notation, we only give the nonzero elements for each of the $\mathbf{M}$ contributions in the following. For that purpose a subscript is at-

tached to the corresponding $f\mathbf{M}$ contribution denoting in which rows (and columns) the nonzero elements are located.

1. Viscous stress

The matrix $\mathbf{M}^\eta$ that reproduces the viscous stress contributions in Eqs. (3), (4), (5) with the closure (6) can be determined by comparison with the classical one-phase hydrodynamic case described in detail in Ref. [4]. Realizing that the contributions in the two-phase model due to viscous stresses are the sum of the single phase contributions, one finds with the aid of Ref. [4]

$$\mathbf{M}^\eta(\mathbf{r})_{\{\mathbf{u},\epsilon_s,\epsilon_l\}}=\begin{pmatrix} \mathbf{M}^\eta_{\mathbf{uu}} & \mathbf{M}^\eta_{\mathbf{u}\epsilon_s} & \mathbf{M}^\eta_{\mathbf{u}\epsilon_l} \\ \mathbf{M}^\eta_{\epsilon_s\mathbf{u}} & M^\eta_{\epsilon_s\epsilon_s} & 0 \\ \mathbf{M}^\eta_{\epsilon_l\mathbf{u}} & 0 & M^\eta_{\epsilon_l\epsilon_l} \end{pmatrix}, \qquad (42)$$

with

$$\mathbf{M}^\eta_{\mathbf{uu}}=-[\boldsymbol{\nabla}(\breve{\eta}_s+\breve{\eta}_l)\boldsymbol{\nabla}+\mathbf{1}\boldsymbol{\nabla}\cdot(\breve{\eta}_s+\breve{\eta}_l)\boldsymbol{\nabla}]^T-2\boldsymbol{\nabla}(\breve{\kappa}_s+\breve{\kappa}_l)\boldsymbol{\nabla}, \tag{43}$$

$$\mathbf{M}^\eta_{\mathbf{u}\epsilon_s}=\boldsymbol{\nabla}\cdot\breve{\eta}_s\dot{\boldsymbol{\gamma}}+\boldsymbol{\nabla}\breve{\kappa}_s\,\mathrm{tr}\,\dot{\boldsymbol{\gamma}}, \tag{44}$$

$$\mathbf{M}^\eta_{\epsilon_s\mathbf{u}}=-\breve{\eta}_s\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\nabla}-\breve{\kappa}_s\,\mathrm{tr}\,\dot{\boldsymbol{\gamma}}\boldsymbol{\nabla}, \tag{45}$$

$$M^\eta_{\epsilon_s\epsilon_s}=\frac{1}{2}\breve{\eta}_s\dot{\boldsymbol{\gamma}}{:}\dot{\boldsymbol{\gamma}}+\frac{1}{2}\breve{\kappa}_s(\mathrm{tr}\,\dot{\boldsymbol{\gamma}})^2, \tag{46}$$

$$\mathbf{M}^\eta_{\mathbf{u}\epsilon_l}=\boldsymbol{\nabla}\cdot\breve{\eta}_l\dot{\boldsymbol{\gamma}}+\boldsymbol{\nabla}\breve{\kappa}_l\,\mathrm{tr}\,\dot{\boldsymbol{\gamma}}, \tag{47}$$

$$\mathbf{M}^\eta_{\epsilon_l\mathbf{u}}=-\breve{\eta}_l\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\nabla}-\breve{\kappa}_l\,\mathrm{tr}\,\dot{\boldsymbol{\gamma}}\boldsymbol{\nabla}, \tag{48}$$

$$M^\eta_{\epsilon_l\epsilon_l}=\frac{1}{2}\breve{\eta}_l\dot{\boldsymbol{\gamma}}{:}\dot{\boldsymbol{\gamma}}+\frac{1}{2}\breve{\kappa}_l(\mathrm{tr}\,\dot{\boldsymbol{\gamma}})^2, \tag{49}$$

and

$$\dot{\boldsymbol{\gamma}}=\boldsymbol{\nabla}\mathbf{v}+[\boldsymbol{\nabla}\mathbf{v}]^T, \tag{50}$$

$$\breve{\eta}_s=\eta_s\phi T_s, \tag{51}$$

$$\breve{\eta}_l=\eta_l(1-\phi)T_l, \tag{52}$$

$$\breve{\kappa}_s=\hat{\kappa}_s\phi T_s, \tag{53}$$

$$\breve{\kappa}_l=\hat{\kappa}_l(1-\phi)T_l. \tag{54}$$

By calculating $\mathbf{M}^\eta(\mathbf{r})\cdot\delta S/\delta\mathbf{x}(\mathbf{r})$ one indeed recovers the desired terms in Eqs. (3), (4), (5). Furthermore, one can show that the matrix $\mathbf{M}^\eta$ given by Eq. (42) is symmetric, positive semidefinite and fulfills the degeneracy requirement (25).

2. Heat conduction: Bulk contribution

Analogously to the discussion for the viscous stress contribution, one can determine the irreversible contributions due to the bulk heat flows in Eqs. (4), (5) using the closure (7). The resulting matrix

$$\mathbf{M}^\lambda(\mathbf{r})_{\{\epsilon_s,\epsilon_l\}}=-\begin{pmatrix} \boldsymbol{\nabla}\cdot\boldsymbol{\lambda}_s\phi T_s^2\cdot\boldsymbol{\nabla} & 0 \\ 0 & \boldsymbol{\nabla}\cdot\boldsymbol{\lambda}_l(1-\phi)T_l^2\cdot\boldsymbol{\nabla} \end{pmatrix} \tag{55}$$

is symmetric, positive semidefinite, respects the degeneracy (25) and by $\mathbf{M}^\lambda(\mathbf{r})\cdot\delta S/\delta\mathbf{x}(\mathbf{r})$ leads to the desired heat flux contributions.

3. Heat conduction: Interface contribution

Since the heat flux through the interface is specific to two-phase systems, we cannot here resort to one-phase hydrodynamics to find the proper contributions ϵ_α^q given by Eq. (9) to the Eqs. (4), (5). Since the expressions ϵ_α^q contain the temperatures T_s, T_l, and T_i, inspection of $\delta S/\delta\mathbf{x}$ suggests that only the elements in the rows and columns ϵ_s, ϵ_l, and ϵ_i are nonzero. Indeed, the matrix $\mathbf{M}^q$ defined by

$$\mathbf{M}^q(\mathbf{r})_{\{\epsilon_s,\epsilon_l,\epsilon_i\}}$$

$$=\psi T_i\begin{pmatrix} \dfrac{\lambda_s^{(0)}}{l_s^{(0)}}T_s & 0 & -\dfrac{\lambda_s^{(0)}}{l_s^{(0)}}T_s \\[3mm] 0 & \dfrac{\lambda_l^{(0)}}{l_l^{(0)}}T_l & -\dfrac{\lambda_l^{(0)}}{l_l^{(0)}}T_l \\[3mm] -\dfrac{\lambda_s^{(0)}}{l_s^{(0)}}T_s & -\dfrac{\lambda_l^{(0)}}{l_l^{(0)}}T_l & \left(\dfrac{\lambda_s^{(0)}}{l_s^{(0)}}T_s+\dfrac{\lambda_l^{(0)}}{l_l^{(0)}}T_l\right) \end{pmatrix} \tag{56}$$

is symmetric, positive semidefinite, respects the degeneracy requirement, and results by $\mathbf{M}^q(\mathbf{r})\cdot\delta S/\delta\mathbf{x}(\mathbf{r})$ in the desired heat transfer contributions. In addition, the degeneracy requirement produced a corresponding contribution in the equation for the internal energy of the interface ϵ_i, such that the total energy is conserved by the interfacial heat transfer.

4. Phase change contributions

Here, we try to model the contributions to the evolution Eqs. (1)–(5), (17)–(20) arising due to phase change. It has been observed in many applications of the GENERIC framework (and is a fundamental essence thereof) that the appearances of one and the same phenomena in the different evolution equations are interwoven. In order to address this question for the phase change contribution when unifying the two-phase model with the Schneider rate equations, we first consider a wider class of closures for the phase change contributions than presented in Sec. I A in a twofold sense. First, we allow arbitrary sources for the phase transformation rates in the structural variables Φ_μ of the form

$$\dot{\Phi}_\mu\big|_{\mathrm{pc}}=\Upsilon_\mu(\mathbf{x}) \quad (\mu=1,2,3,4), \tag{57}$$

generalizing the modified Schneider rate Eqs. (17)–(20), where we have used $\{\Phi_1, \Phi_2, \Phi_3, \Phi_4\} \equiv \{\phi, \psi, \Psi_2, \Psi_3\}$ to simplify the notation. Second, the rate of phase change of any of the structural variables Φ_μ may enter in any other balance equation in the sense

$$\frac{\partial \mathbf{x}}{\partial t} = \cdots + \sum_{\mu=1}^4 \mathbf{a}_\mu \Upsilon_\mu(\mathbf{x}). \tag{58}$$

It is essential for the further procedure to notice that by virtue of Eqs. (57) and (58), the set of vectors $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4\}$, representing the effect of phase change in terms of $\{\Phi_1, \Phi_2, \Phi_3, \Phi_4\}$ on all variables $\mathbf{x}$, is linearly independent as inspection of their four last components shows

$$\mathbf{a}_1 = \begin{pmatrix} \vdots \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \mathbf{a}_2 = \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad \mathbf{a}_3 = \begin{pmatrix} \vdots \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \quad \mathbf{a}_4 = \begin{pmatrix} \vdots \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{59}$$

representing the four Eqs. (57). If we assume that the phase change terms can be formulated in GENERIC, one may write

$$\dot{\Phi}_\mu|_{\mathrm{pc}} = \Upsilon_\mu = \mathbf{b}_\mu \cdot \frac{\delta S}{\delta \mathbf{x}} \quad (\mu = 1,2,3,4). \tag{60}$$

Then the matrix $\mathbf{M}^{\mathrm{pc}}$ describing the phase change contributions becomes due to Eq. (58)

$$\mathbf{M}^{\mathrm{pc}} = \sum_{\mu=1}^4 \mathbf{a}_\mu \mathbf{b}_\mu. \tag{61}$$

In the following, we make the basic assumption that $\mathbf{M}^{\mathrm{pc}} \cdot \delta S/\delta \mathbf{x}$ is an ordinary matrix multiplication, i.e., that no part of the operator acts as a derivative or as an integration. Thus, the vectors $\mathbf{a}_\mu$ and $\mathbf{b}_\mu$ are ''normal'' vectors. The task to formulate the phase change terms in GENERIC then becomes a matter of linear algebra. Due to the fact that the vectors $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4\}$ are linearly independent, one can show in a mathematically rigorous manner that the matrix $\mathbf{M}^{\mathrm{pc}}$ is symmetric and positive semidefinite *if and only if*

$$\mathbf{M}^{\mathrm{pc}} = \sum_{\mu,\nu=1}^4 A_{\mu\nu} \mathbf{a}_\mu \mathbf{a}_\nu, \tag{62}$$

with

$$\mathbf{A} = [A_{\mu\nu}] \geq \mathbf{0}, \tag{63}$$

$$\mathbf{A}^T = \mathbf{A}, \quad \text{i.e.,} \quad A_{\mu\nu} = A_{\nu\mu}. \tag{64}$$

Equation (62) emphasizes that the driving forces for the phase change as introduced in Eq. (60) are intimately coupled to the appearance of the phase change contributions in the evolution equations, namely to the vectors $\mathbf{a}_\mu$, by $\mathbf{b}_\mu = \Sigma_\nu A_{\mu\nu} \mathbf{a}_\nu$. Furthermore, if we define

$$\Lambda_\nu^{(E)} \equiv \mathbf{a}_\nu \cdot \frac{\delta E}{\delta \mathbf{x}} \quad (\nu = 1,2,3,4), \tag{65}$$

$$\Lambda_\nu^{(S)} \equiv \mathbf{a}_\nu \cdot \frac{\delta S}{\delta \mathbf{x}} \quad (\nu = 1,2,3,4), \tag{66}$$

the degeneracy requirement (25) and the equations of motion for the structural variables read

$$0 = \sum_{\nu=1}^4 A_{\mu\nu}(\mathbf{x}) \Lambda_\nu^{(E)}(\mathbf{x}) \quad (\mu = 1,2,3,4), \tag{67}$$

$$\dot{\Phi}_\mu|_{\mathrm{pc}} = \sum_{\nu=1}^4 A_{\mu\nu}(\mathbf{x}) \Lambda_\nu^{(S)}(\mathbf{x}) \quad (\mu = 1,2,3,4). \tag{68}$$

The set of Eqs. (62)–(68) contains the necessary and sufficient conditions for the phase change contributions in Eq. (58) under the restrictions discussed after Eq. (61). In the following, we attempt to specify the matrix $[A_{\mu\nu}]$ for the equations of motions (1)–(5). First, we identify the vectors $\mathbf{a}_\mu$ with the corresponding contributions in Eqs. (1)–(5). The fact that the evolution equations for the mass density of the interface and for the internal energy density of the interface, and hence, also their phase change contributions, are unspecified, leaves the corresponding components of the four vectors $\mathbf{a}_\mu$ undetermined, apart from the degeneracy requirement (67). However, as shown in the Appendix, the only physically meaningful choice of the corresponding components of $\mathbf{a}_\mu$ is such that $\mathbf{\Lambda}^{(E)} = \mathbf{0}$. If one assumes that Ψ_2 and Ψ_3 have no influence on the balance equations of ρ_i and ϵ_i [i.e., if $(\mathbf{a}_3)_{\rho_i} = (\mathbf{a}_4)_{\rho_i} = (\mathbf{a}_3)_{\epsilon_i} = (\mathbf{a}_4)_{\epsilon_i} = 0$], and using total mass conservation [which by virtue of Eqs. (1), (2) results in $(\mathbf{a}_1)_{\rho_i} = (\mathbf{a}_2)_{\rho_i} = 0$], one concludes from $\mathbf{\Lambda}^{(E)} = \mathbf{0}$ and Eqs. (4), (5) that $(\mathbf{a}_1)_{\epsilon_i} = -(\epsilon_s^\Gamma - \epsilon_l^\Gamma)$ and $(\mathbf{a}_2)_{\epsilon_i} = 0$. Since, by doing so, all components of the four vectors $\mathbf{a}_\mu$ are determined, one finds

$$\mathbf{a}_1 = \begin{pmatrix} \hat{\rho} \\ -\hat{\rho} \\ 0 \\ 0 \\ \epsilon_s^\Gamma \\ -\epsilon_l^\Gamma \\ -(\epsilon_s^\Gamma - \epsilon_l^\Gamma) \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad \mathbf{a}_2 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad \mathbf{a}_3 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \quad \mathbf{a}_4 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \tag{69}$$

and hence with $\delta S/\delta \mathbf{x}$ from Eq. (38) and $\sigma = -\tilde{p}_i$

$$\mathbf{\Lambda}^{(S)} = \begin{pmatrix} \epsilon_s^{\Gamma}\left(\dfrac{1}{T_s}-\dfrac{1}{T_i}\right)+\epsilon_l^{\Gamma}\left(\dfrac{1}{T_i}-\dfrac{1}{T_l}\right)-\hat{\rho}\left(\dfrac{\mu_s}{T_s}-\dfrac{\mu_l}{T_l}\right)+\left(\dfrac{\tilde{p}_s}{T_s}-\dfrac{\tilde{p}_l}{T_l}\right) \\ -\dfrac{\sigma}{T_i} \\ 0 \\ 0 \end{pmatrix}. \tag{70}$$

By combining the evolution equation of the volume fraction (17) with eq. (68),

$$\dot{\phi}|_{\text{pc}} = G\psi = (A_{11}\Lambda_1^{(S)}+A_{12}\Lambda_2^{(S)}) \equiv \psi(\tilde{A}_{11}\Lambda_1^{(S)}+\tilde{A}_{12}\Lambda_2^{(S)}), \tag{71}$$

and by assuming the same thermodynamic driving forces for $\dot{\phi}|_{\text{pc}}\,(=\dot{\Phi}_1|_{\text{pc}})$, $\dot{\psi}|_{\text{pc}}\,(=\dot{\Phi}_2|_{\text{pc}})$, and for $\dot{\Psi}_2|_{\text{pc}}\,(=\dot{\Phi}_3|_{\text{pc}})$ as proposed by the Schneider Eqs. (17)–(19), the matrix $\mathbf{A}$ is found to be of the form (the star symbols denote elements that are not yet determined)

$$\mathbf{A} = \begin{pmatrix} \psi\tilde{A}_{11} & \psi\tilde{A}_{12} & \star & \star \\ \mathcal{L}\tilde{A}_{11} & \mathcal{L}\tilde{A}_{12} & \star & \star \\ \Psi_3\tilde{A}_{11} & \Psi_3\tilde{A}_{12} & \star & \star \\ \star & \star & \star & \star \end{pmatrix}, \tag{72}$$

which, due to symmetry, becomes (setting $\mathcal{R}\equiv\tilde{A}_{11}$)

$$\mathbf{A} = \frac{\mathcal{R}(\mathbf{x})}{\psi}\begin{pmatrix} \psi^2 & \psi\mathcal{L} & \psi\Psi_3 & \star \\ \psi\mathcal{L} & \mathcal{L}^2 & \Psi_3\mathcal{L} & \star \\ \psi\Psi_3 & \Psi_3\mathcal{L} & \star & \star \\ \star & \star & \star & \star \end{pmatrix}, \tag{73}$$

with the rate "constant" $\mathcal{R}(\mathbf{x})[\text{K m}^4\text{ J}^{-1}\text{ s}^{-1}]$. The positive semidefiniteness of $\mathbf{A}$ implies $\mathcal{R}(\mathbf{x})\geq 0\,\forall\,\mathbf{x}$. Through the explicit construction of the Choleski decomposition for the matrix $\mathbf{A}$ with the matrix elements already specified in Eq. (73), it can be shown rigorously that the relation $\mathcal{L}A_{14}=\psi A_{24}$ must hold. The other four elements in the lower-right corner, which do not contribute to the dynamics, remain undetermined except that $\mathbf{A}$ must be symmetric and positive semidefinite. The matrix $\mathbf{A}$ then takes the form

$$\mathbf{A} = \frac{\mathcal{R}(\mathbf{x})}{\psi}\begin{pmatrix} \psi^2 & \psi\mathcal{L} & \psi\Psi_3 & \psi\mathcal{Q}(\underline{f}\mathbf{x}) \\ \psi\mathcal{L} & \mathcal{L}^2 & \mathcal{L}\Psi_3 & \mathcal{L}\mathcal{Q}(\mathbf{x}) \\ \psi\Psi_3 & \mathcal{L}\Psi_3 & \star & \star \\ \psi\mathcal{Q}(\mathbf{x}) & \mathcal{L}\mathcal{Q}(\mathbf{x}) & \star & \star \end{pmatrix}, \tag{74}$$

where $\mathcal{Q}(\mathbf{x})\,[\text{m}^{-4}]$ is an unspecified function. According to the phase change expressions for the structural variables given in the modified Schneider rate Eqs. (17)–(20) and with Eq. (68) one finds for the radial growth rate G and for the nucleation rate α

$$G = \mathcal{R}\left(\Lambda_1^{(S)}+\frac{\mathcal{L}}{\psi}\Lambda_2^{(S)}\right), \tag{75}$$

$$8\pi\alpha = \mathcal{R}\mathcal{Q}\left(\Lambda_1^{(S)}+\frac{\mathcal{L}}{\psi}\Lambda_2^{(S)}\right). \tag{76}$$

Let us first comment on the expression (75) for radial growth rate G. Using the functional derivatives of the entropy given in Eq. (38) and with the definition of the vector $\mathbf{\Lambda}^{(S)}$ (66) one finds

$$\frac{G}{\mathcal{R}} = \Lambda_1^{(S)}+\frac{\mathcal{L}}{\psi}\Lambda_2^{(S)} = \hat{\rho}\bar{h}_{si}\left(\frac{1}{T_s}-\frac{1}{T_i}\right)+\hat{\rho}\bar{h}_{li}\left(\frac{1}{T_i}-\frac{1}{T_l}\right)$$

$$-\hat{\rho}\left(\frac{\mu_s}{T_s}-\frac{\mu_l}{T_l}\right)+\frac{1}{\psi}\frac{1}{T_i}\,(\psi[\tilde{p}_s-\tilde{p}_l]-\mathcal{L}\sigma), \tag{77}$$

where we have set the interfacial pressures equal to the bulk pressures, $\tilde{p}_{\alpha i}=\tilde{p}_{\alpha}$, in agreement with the discussion after Eq. (10) and the comments after Eq. (32), and the last term in parentheses is the "Laplace" contribution. It is striking to see that the phase change is equally driven by the phase differences of all three intensive variables, namely temperature, chemical potential, and pressure. In particular, the "Laplace" contribution in Eq. (77) is worth a comment. In a microscopic description of the interface, the Laplace equation relates the pressure difference to the surface tension by equating the change in volume times the pressure difference to the change in surface times the surface tension. Since, according to the Schneider Eqs. (17), (18), ψ and $\mathcal{L}$ are the relevant quantities for change in volume fraction and in surface per volume, respectively, the last contribution in Eq. (77) is the most natural and appropriate formulation of the Laplace equation for the coarse grained description adopted in this paper. Furthermore, Eq. (77) shows that the beyond-equilibrium situation in terms of a deviation from the recast Laplace equation is a driving force for phase change. The expression (77) for the radial growth rate may be used to study the influence of the microstructure on the melting temperature $T^{\star}$. If the latter is defined by $G=0$ and $T_s=T_l=T_i\equiv T^{\star}$, the corresponding criterion reads

$$-\hat{\rho}(\mu_s-\mu_l)+\left([\tilde{p}_s-\tilde{p}_l]-\frac{\mathcal{L}}{\psi}\sigma\right)=0. \tag{78}$$

We notice that the microstructure enters through the prefactor $\mathcal{L}/\psi\,[\text{m}^{-1}]$ of the surface tension, which becomes impor-

tant for very small spherulites. If the independent variables in Eq. (78) are the melting temperature $T^\star$, the pressures $\tilde{p}_s$ and $\tilde{p}_l$, and the inverse length $\mathcal{L}/\psi$, Eq. (78) predicts the change in the melting temperature when changing the spherulite size, i.e., the melting temperature depression (see also, e.g., Ref. [25]). Finally, one should notice that as far as temperature and pressure is concerned, the corresponding quantities of the interface T_i and σ enter in Eq. (77), which is in clear contrast to the chemical potential, where the influence of the interfacial property μ_i is absent. This asymmetry originates from the fact that in the current model, the interfacial mass density ρ_i is not influenced by the phase change of any of the structural variables, i.e., from $(\mathbf{a}_\mu)_{\rho_i} = 0 \; \forall \mu$. However, in view of the procedure presented above, the effect of phase change contributions in the balance equation for ρ_i on the radial growth rate (77) may be elaborated straightforwardly.

A comparison of the expressions for the radial growth rate G (75) and for the nucleation rate α (76) results in

$$8\pi\alpha = \mathcal{Q}G. \tag{79}$$

It is of fundamental importance to notice that this does *not* necessarily mean that the nucleation rate α is essentially the same driving force as the radial growth rate G, since the function $\mathcal{Q} = \mathcal{Q}(\mathbf{x})$ introduced in Eq. (74) is an arbitrary function. Thus, the GENERIC formalism does not impose any constraint on the form of the nucleation rate except that the roots of the function G must also be roots of the function α in order to have a nondiverging $\mathcal{Q}$, and correspondingly nondiverging elements in the matrices $\mathbf{A}$ (74) and finally $\mathbf{M}^{\mathrm{pc}}$ (62). Physically speaking, this implies that for conditions under which the radial growth rate is zero the nucleation rate must vanish. Hence, the distinction between nucleation and growth becomes obliterate under such ''steady-state'' conditions. It is worthwhile to notice that this constraint from the GENERIC formalism on α is much weaker than the restrictions imposed on the form of G as given in Eqs. (75), (77) since in the latter case the function $\mathcal{R}$ must obey $\mathcal{R} \geq 0$. This is insofar a severe restriction, as in particular, $\mathcal{R}$ cannot account for the different signs of the radial growth rate G in melting and crystallization conditions, respectively.

D. Final set of equations

We collect here the previously discussed building blocks of the GENERIC formalism in order to write down the final set of equations describing the two-phase flow, including the interface, in conjunction with the Schneider rate equations. At this point, the reader should notice the implications of the GENERIC structure on the equations for the mass density of the interface and for the internal energy density of the interface. First, the reversible contributions given by the elements $\mathbf{L}_{\rho_i \mathbf{u}}$ and $\mathbf{L}_{\epsilon_i \mathbf{u}}$ defined in Eq. (40) emerged not only due to analogy with $\{\rho_s, \rho_l\}$ and $\{\epsilon_s, \epsilon_l\}$, respectively, but also due to the GENERIC conditions imposed on $\mathbf{L}$. Second, the irreversible contributions due to heat transfer across the interface and due to phase change naturally (although not completely rigorously in the latter case) arose from the conditions im-

posed on $\mathbf{M}$. Using the expressions for the functional derivatives of E and of S given in Eq. (38), and for the operators $\mathbf{L}$ (39) and $\mathbf{M}$ (41), the final and complete set of equations describing the two-phase flow, including the dynamics of the interface and the Schneider rate equations, reads

$$\partial_t \rho_s + \boldsymbol{\nabla} \cdot (\mathbf{v}\rho_s) = +\hat{\rho}G\psi, \tag{80}$$

$$\partial_t \rho_l + \boldsymbol{\nabla} \cdot (\mathbf{v}\rho_l) = -\hat{\rho}G\psi, \tag{81}$$

$$\partial_t \rho_i + \boldsymbol{\nabla} \cdot (\mathbf{v}\rho_i) = 0, \tag{82}$$

$$\partial_t \mathbf{u} + \boldsymbol{\nabla} \cdot (\mathbf{v}\mathbf{u}) = -\boldsymbol{\nabla}(p_s + p_l) + \boldsymbol{\nabla} \cdot (\boldsymbol{\tau}_s + \boldsymbol{\tau}_l) + \boldsymbol{\nabla}(\tfrac{2}{3}\psi\sigma), \tag{83}$$

$$\partial_t \epsilon_s + \boldsymbol{\nabla} \cdot (\mathbf{v}\epsilon_s) = -p_s(\boldsymbol{\nabla} \cdot \mathbf{v}) + \boldsymbol{\tau}_s : (\boldsymbol{\nabla}\mathbf{v}) - \boldsymbol{\nabla} \cdot \mathbf{q}_s + \epsilon_s^q + \epsilon_s^\Gamma G\psi, \tag{84}$$

$$\partial_t \epsilon_l + \boldsymbol{\nabla} \cdot (\mathbf{v}\epsilon_l) = -p_l(\boldsymbol{\nabla} \cdot \mathbf{v}) + \boldsymbol{\tau}_l : (\boldsymbol{\nabla}\mathbf{v}) - \boldsymbol{\nabla} \cdot \mathbf{q}_l + \epsilon_l^q - \epsilon_l^\Gamma G\psi, \tag{85}$$

$$\partial_t \epsilon_i + \boldsymbol{\nabla} \cdot (\mathbf{v}\epsilon_i) = \tfrac{2}{3}\psi\sigma(\boldsymbol{\nabla} \cdot \mathbf{v}) - (\epsilon_s^q + \epsilon_l^q) - (\epsilon_s^\Gamma - \epsilon_l^\Gamma)G\psi, \tag{86}$$

$$\partial_t \phi + \mathbf{v} \cdot \boldsymbol{\nabla}\phi = G\psi, \tag{87}$$

$$\partial_t \psi + \mathbf{v} \cdot \boldsymbol{\nabla}\psi + \tfrac{1}{3}\psi(\boldsymbol{\nabla} \cdot \mathbf{v}) = G\mathcal{L}(\phi, \psi, \Psi_2), \tag{88}$$

$$\partial_t \Psi_2 + \boldsymbol{\nabla} \cdot (\mathbf{v}\Psi_2) - \tfrac{1}{3}\Psi_2(\boldsymbol{\nabla} \cdot \mathbf{v}) = G\Psi_3, \tag{89}$$

$$\partial_t \Psi_3 + \boldsymbol{\nabla} \cdot (\mathbf{v}\Psi_3) = 8\pi\alpha, \tag{90}$$

where the expressions for $\mathcal{L}$ and G are given in Eqs. (22) and (77), respectively, and where the roots of the function $G(\mathbf{x})$ needs to be roots of $\alpha(\mathbf{x})$.

III. SUMMARY

The solid-liquid two-phase model given by the Eqs. (1)–(5) has been united with the Schneider rate Eqs. (17)–(20) within the GENERIC framework of beyond-equilibrium thermodynamics in order to describe the dynamics of solidification, resulting in Eqs. (80)–(90). The dynamic equations for the thermodynamic variables of the interface have been constructed using GENERIC as a guideline. It has been shown that dissipative contributions due to the viscous stresses and to the heat fluxes in both phases, as well as the heat exchange across the interface could be incorporated. Furthermore, according to the GENERIC formalism the radial growth rate in the Schneider rate equations is not an additional material function but is expressed in terms of the phase differences in temperature, chemical potential, and pressure as shown in Eq. (77). It has been discussed that this expression for the radial growth factor naturally incorporates the dependence on the crystallite size due to the surface tension in terms of a reformulated Laplace equation. Thus, it may be used to examine the dependence of the melting temperature on the microstructure. Finally, it is found that for conditions under which the radial growth rate is zero the nucleation rate must vanish.

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APPENDIX

In this appendix, it is shown why the phase change contributions in the equations for the mass density ρ_i and for the internal energy density ϵ_i of the interface are most naturally chosen such that $\mathbf{\Lambda}^{(E)} \equiv_f \mathbf{0}$. If we assume that there is no contribution in the equation for ρ_i and for ϵ_i due to the change in the structural variables Ψ_2 and Ψ_3, it follows from the form of the functional derivative $\delta E/\delta \mathbf{x}$ (38), from the two-phase flow Eqs. (1)–(5) and from the definition of $\mathbf{\Lambda}^{(E)}$ (65) that $\Lambda_3^{(E)}=0$ and $\Lambda_4^{(E)}=0$. In order to fulfill the degeneracy condition, four cases then need to be considered:

$$\text{Case 1:} \quad \{\Lambda_1^{(E)} \neq 0, \ \Lambda_2^{(E)}=0\},$$

$$\text{Case 2:} \quad \{\Lambda_1^{(E)}=0, \ \Lambda_2^{(E)} \neq 0\},$$

$$\text{Case 3:} \quad \{\Lambda_1^{(E)} \neq 0, \ \Lambda_2^{(E)} \neq 0\},$$

$$\text{Case 4:} \quad \{\Lambda_1^{(E)}=0, \ \Lambda_2^{(E)}=0\}.$$

In the first case, one finds that the first column and row in the symmetric matrix $\mathbf{A}$ must be zero, resulting in $D_t\Phi_1=D_t\phi=0$. Accordingly, the second case leads to $D_t\Phi_2=D_t\psi=0$. Hence, the first two cases can be discarded. In the third case, the symmetric matrix $\mathbf{A}$ must be of the form

$$\mathbf{A}=\begin{pmatrix} \beta\Lambda_2^{(E)} & -\beta\Lambda_1^{(E)} & \star & \star \\ -\beta\Lambda_1^{(E)} & \star & \star & \star \\ \star & \star & \star & \star \\ \star & \star & \star & \star \end{pmatrix}. \tag{A1}$$

However, according to the Schneider Eqs. (17), (18), the ratio $D_t\phi/D_t\psi$ determined via Eq. (68) should only depend on the microstructure. It is very possible that this can be achieved but only with a very peculiar choice for the matrix element A_{22}. The fourth case does not put any constraints on the matrix $\mathbf{A}$ and is hence considered to be the appropriate condition to determine the missing ϵ_i-components of the vectors $\{\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3,\mathbf{a}_4\}$. Physically, the fourth case expresses the fact that the total energy is conserved by change in each of the structural variables individually, whereas the third case requires a subtle balance of the phase change in volume fraction and interfacial area to respect total-energy conservation.

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[1] M. Ishii, *Thermo-Fluid Dynamic Theory of Two-Phase Flow* (Eyrolles, Paris, 1975).

[2] W. Schneider, A. Köppel, and J. Berger, Int. Polym. Process. **2**, 151 (1988).

[3] M. Grmela and H. C. Öttinger, Phys. Rev. E **56**, 6620 (1997).

[4] H. C. Öttinger and M. Grmela, Phys. Rev. E **56**, 6633 (1997).

[5] D. A. Drew and S. L. Passman, *Theory of Multicomponent Fluids* (Springer, New York, 1999).

[6] J. Ni and C. Beckermann, Metall. Trans. B **22**, 349 (1991).

[7] H. Enwald E. Peirano, and A.-E. Almstedt, Int. J. Multiphase Flow **22** (Suppl.), 21 (1996).

[8] D. A. Drew, Annu. Rev. Fluid Mech. **15**, 261 (1983).

[9] M. Avrami, J. Chem. Phys. **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).

[10] M. C. Tobin, J. Polym. Sci., Polym. Phys. Ed. **12**, 399 (1974); **14**, 2253 (1976).

[11] G. Eder, H. Janeschitz-Kriegl, and S. Liedauer, Prog. Polym. Sci. **15**, 629 (1990).

[12] G. Eder, Nonlinear Anal. Theor. **30**, 3807 (1997).

[13] G. Eder, in *Proceedings of the ASME Heat Transfer Division, Dallas, Texas, 1997*, edited by D. A. Zumbrunnen *et al.* (Dallas, Texas, 1997), p. 131.

[14] G. Eder and H. Janeschitz-Kriegl, in *Materials Science and Technology*, edited by H. Meijer (Wiley-VCH, Weinheim, 1997), Vol. 18, p. 269.

[15] G. Eder, in *Macromolecular Desing of Polymeric Materials*, edited by K. Hatada and T. Kitayama and O. Vogel (Dekker, New York, 1997), p. 761.

[16] H. C. Öttinger, Phys. Rev. E **57**, 1416 (1998).

[17] H. C. Öttinger, Phys. Rev. E **62**, 4720 (2000).

[18] H. B. Stewart and B. Wendroff, J. Comput. Phys. **56**, 363 (1984).

[19] D. D. Holm and B. A. Kupershmidt, Int. J. Multiphase Flow **12**, 681 (1986).

[20] C. M. Hsiung and M. Cakmak, Polym. Eng. Sci. **31**, 1372 (1991).

[21] X. Guo, A. I. Isayev, and L. Guo, Polym. Eng. Sci. **39**, 2096 (1999).

[22] C. Morel, N. Goreaud, and J.-M. Delhaye, Int. J. Multiphase Flow **25**, 1099 (1999).

[23] N. J. Wagner, H. C. Öttinger, and B. J. Edwards, AIChE J. **45**, 1169 (1999).

[24] M. Doi and T. Ohta, J. Chem. Phys. **95**, 1242 (1991).

[25] R. Defay and I. Prigogine and A. Bellemans, *Surface Tension and Adsorption* (Longmans, Green, London, 1966).