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GENERIC model for multiphase systems

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ABSTRACT

GENERIC is a nonequilibrium thermodynamic formalism in which the dynamic behavior of a system is described by a single compact equation involving two types of brackets: a Poisson bracket and a dissipative bracket. This formalism has proved to be a very powerful instrument to model the dynamic behavior of complex bulk phases. In this paper we review the basic principles of the GENERIC formalism, and show how it can be applied to multicomponent multiphase systems with interfaces displaying viscous stress deformation behavior. The generalization of the GENERIC formalism to multiphase systems provides a powerful tool to model nonlinear dynamic behavior of complex interfaces in for example emulsions or foam. Adding several interfacial contributions to the standard two-bracket formulation we derive the conservation laws for mass, momentum, and energy for the bulk phases of the system. We also derive the jump balance equations for the surface mass density, surface momentum, and surface energy. In addition to these balance equations we obtain constitutive equations for the extra stress tensor, energy flux vector, and mass flux vectors in the bulk phase, and the surface extra stress tensor, the surface energy flux vector, and surface mass flux vectors of the interface. The GENERIC formalism also allows us to derive constitutive equations for the transport of mass, momentum, and energy from the bulk phase to the interface. The resulting set of equations is compared to those derived using the rational thermodynamic and classical irreversible thermodynamic formalisms, and is in good agreement with the balance equations derived using these formalisms.

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1. Introduction

In multicomponent multiphase systems surface rheology, surface diffusion, surface heat conduction, and transfer of mass, momentum and energy across the phase interfaces can have a significant effect on the overall dynamics of a system [1–4]. For example, the dynamics of vesicles and microcapsules in a flow field are highly affected by surface rheology and mass transfer across the interface [5]. Surface rheology and mass transfer (both in-plane and perpendicular to the interface) also affect the amplitude of surface waves [6,7], the stability of foam [8], the stability of emulsions [9,10], the wetting behavior of thin films on solid surfaces [11], or the dynamics of biological systems [12].

The transport of mass, momentum, and energy along and across interfaces can be modelled by incorporating excess surface variables, such as a surface mass density, surface momentum density, surface energy, and surface entropy in the continuum description of a system [1–4]. This leads to a set of differential balance equations for these excess variables, which serve as boundary conditions for the balance equations for the bulk fields. Apart from the familiar constitutive equations for the bulk stress tensor, bulk energy flux vector, and mass flux vectors for the various species in the bulk phase, we need to close the set of equations by specifying constitutive equations for the surface fluxes: the surface stress tensor, the surface energy flux vector,

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and the surface mass flux vectors [1–4]. When specifying these constitutive equations the entropy production in the system is generally used as a guide [13].

Such a nonequilibrium thermodynamic approach, based on either classical irreversible thermodynamics (CIT) or rational thermodynamics (RT), leads to linear constitutive equations, which are basically the surface equivalents of the Newtonian fluid model, Fourier's law, and Fick's law [1–4].These linear relations are valid only for small departures from equilibrium. In many practical application, for example the production or processing of emulsions, systems are far from equilibrium, and linear relations such as the linear Boussinesq model for the stress tensor [14] give rather poor predictions of the stress deformation behavior of the interfaces. For a more adequate description of the behavior of the interfaces far from equilibrium, nonlinear models are needed. Nonequilibrium formalisms such as classical irreversible thermodynamics or rational thermodynamics are not well suited for the development of such models.

Recently the extended irreversible thermodynamic (EIT) formalism [15,16] was extended to multicomponent multiphase systems with viscoelastic interfaces [17]. In the EIT formalism the assumption of local equilibrium (a key assumption in both CIT and RT) is relaxed, and the entropy is allowed to depend on the local fluxes in the system: the symmetric part of the extra stress tensor, the trace of this tensor, the heat flux vector, and the mass flux vectors [15,16]. The EIT formalism provides a convenient tool to construct co-rotational or upper-convected Maxwell type models for the surface stress tensor. In reference [17] this formalism was used to construct the surface equivalent of the Giesekus model [18]. Although the latter is a nonlinear model it is still valid only for relatively small departures from equilibrium.

A nonequilibrium thermodynamic formalism ideally suited for developing nonlinear constitutive equations, that are also valid far from equilibrium, is the GENERIC formalism (General Equation for the Non-Equilibrium Reversible–Irreversible Coupling) [19–21]. The GENERIC formalism describes the dynamics of a system in terms of two types of brackets: Poisson brackets, describing the reversible part of the dynamics, and dissipative brackets, representing the irreversible part of the dynamics [19–21]. Constraints are imposed on both types of brackets which restrict their specific form (see Section 2). One of the strengths of the GENERIC formalism is its modular character [19–21], which means that it is relatively easy to incorporate nonlinear dependencies on structural variables in the description of a system. These are scalar or tensorial variables describing the microstructure of the material. Structural variables can also be included in the classical irreversible thermodynamic or rational thermodynamic formalism, using the internal variables theory (IVT) [22], but in general this inclusion leads to constitutive models which typically are valid only for small deviations from linear material behavior [23,24].

The GENERIC formalism also allows us to construct constitutive equations for the material behavior of the interface that couple this behavior directly to the behavior of the adjoining bulk phases. Consider for example a system in which a liquid crystalline interface (stabilized by amphiphilic rod-like molecules) separates a liquid crystalline bulk phase (also containing rod-like molecules), and an isotropic bulk phase. We would expect that the orientation of the rod-like molecules in the bulk phase close to the interface will affect the orientation of the rod-like molecules in the interface. This coupling should be incorporated in the constitutive equation for the surface orientation tensor. With the CIT, RT or EIT formalisms it is not possible to construct this coupling. Alternatively, we could use the extended rational thermodynamic (ERT) formalism [25,26] to include this effect. But this formalism requires the fluxes in the system to be treated as conserved variables. As we will see in Section 4, the GENERIC formalism introduces this coupling in a far more natural way, without treating fluxes as conserved variables.

The GENERIC formulation has been applied mainly to isolated single phase systems [19–21], where only bulk contributions to the two-bracket formulation are needed to describe the dynamics of the system. Recently, Öttinger et al. [27] introduced a GENERIC formalism for multiphase systems, in the context of bubble growth by exsolution of a dissolved component from an oversaturated solution. This formalism includes interfacial contributions to the Poisson and dissipative brackets, and is valid for systems with invicid interfaces [27]. In their development Öttinger et al. [27] assume that mass does not accumulate at the interface, and that the surface mass density is negligible. Therefore they do not consider the effects of surface rheology, surface diffusion, or surface heat conduction. For the system they are considering this is a more than reasonable assumption. But for many practical multiphase systems, stabilized by (mixtures) of surface active components these effects may not be negligible. For those systems a generalization of the approach of Öttinger et al. [27] is needed that incorporates these effects. Such a generalization is an important step towards the development of GENERIC formulations for multiphase systems with complex interfaces displaying nonlinear material behavior.

In this paper we review the general structure of the GENERIC formulation, and then discuss its application to multicomponent multiphase systems with interfaces displaying viscous surface behavior. Apart from surface rheology we will also include surface diffusion and surface heat conduction in the description. And for the latter processes we will include cross-coupling effects: the Dufour effect (energy fluxes driven by gradients in concentration), and the Soret effect (mass fluxes driven by temperature gradients). Although such effects are in general negligible in the bulk phase, these cross-couplings tend to be very important for transfer processes across the interface [4]. In Section 2 we will first present a review of the GENERIC formalism for isolated single phase systems. In Section 3 we will present the GENERIC formalism for multiphase systems with viscous interfaces. In Section 4 we will compare the results from the GENERIC formalism to those derived by more classical approaches based on irreversible and rational thermodynamics [1–4]. We will also discuss how the formalism presented here can be extended to develop constitutive equations that include dependencies on structural variables.

2. GENERIC formalism for an isolated single phase system

Let us consider an isolated single phase system, consisting of N components. In classical nonequilibrium thermodynamics [13] the dynamic behavior of such a system is described by the equation of continuity, the $(N-1)$ species mass balances, the momentum balance, the energy balance, and a set of constitutive equations for the fluxes in the system (the stress tensor, the energy flux vector, and the mass flux vectors). These constitutive equations must be chosen such that the entropy inequality is satisfied [3,13]. In the GENERIC formulation these $(2N+3)$ equations are replaced by a single compact equation of the form [19–21]

$$\frac{dA}{dt} = \{A,E\} + [A,S] \tag{1}$$

where the Poisson bracket $\{A, E\}$ represents the reversible part of the dynamics of the system; it is defined by [19–21]

$$\{A,E\} \equiv \frac{\delta A(\mathbf{x})}{\delta \mathbf{x}} \cdot \mathbf{L} \cdot \frac{\delta E(\mathbf{x})}{\delta \mathbf{x}}. \tag{2}$$

In this expression $E(\mathbf{x})$ is the Hamiltonian of the system, $\mathbf{x}$ is the vector of independent system variables, and $\mathbf{L}$ is an antisymmetric matrix. The derivatives in this expression are to be interpreted as functional derivatives. The arbitrary observable A is defined as

$$A = \int_R a dV \tag{3}$$