



Fundamentals of two-phase flow by the method of irreversible thermodynamics

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Abstract

The paper explores thermodynamic aspect of modelling two-phase systems by the methods of irreversible thermodynamics in both classical (CIT) and extended (EIT) formulation. The conservation laws for two-phase model-continuum are derived. Then, the entropy production is analysed for two-fluid and homogeneous systems. Different equations of state are taken into consideration, namely that corresponding to the accompanying equilibrium state of physical element and more complex resulting from EIT. Obtained expressions for rate of entropy production per unit volume allow to identify the dissipative mechanisms in the two-phase system and suggest the forms of phenomenological relations to be adopted in the constitutive equations.

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1. Introduction

The fundamentals of two-phase flow through channels are still in dispute. A study of the literature of the subject (Nigmatulin, 1991; Ishii, 1975; Delhayé et al., 1981; Bergles et al., 1981; Hsu and Graham, 1968; Ginoux, 1978; Hewitt and Hall-Taylor, 1970; Tong, 1965) shows that the systems of equations now in use can be classified under two broad headings: *mixture models* and *two-fluid models*. They are based on two distinct descriptions of the two-phase system at “local” scale. Two-fluid models are currently most frequently used. Several models are derived from these.

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Among them there is the model based on the velocity of the centre of volume from which we can derive the drift flux model expressed in terms of the flux velocity (Ishii, 1975). In particular this model reduces to the homogeneous model when the liquid and vapour velocities are equal. The above mentioned models are well known for years and widely described in the literature. Many papers are devoted to the derivation of the balance equations for these models. Relatively few are intended to develop the thermodynamic aspects of modelling two-phase systems. The present paper explores the potential of the so-called irreversible thermodynamics. In this respect we shall follow the exposition of the classical irreversible thermodynamics (CIT) by Meixner and Reik (1959), and of the extended irreversible thermodynamics (EIT) by Jou et al. (2001).

Section 2 introduces some basic aspects of a model considering a coexistence of two distinct phases in any point. This model is proposed for two-phase systems with particles, in particular when non-equilibrium effects are important. For such cases we define the concept of an accompanying equilibrium. Some definitions are given in Section 3. We take account of the inherently non homogeneous nature of the flow system and replace it in Section 4 by a physically equivalent continuum through the application of the Euler–McLaurin approximation of a sum by an integral. In Section 5, we formulate the conservation laws in terms of this model-continuum. The Gibbs equation for the system is written for different equations of state, namely that corresponding to the accompanying equilibrium state of a physical element, as proposed by Bataille and Kestin (1975, 1977), Kestin (1979) and other much more complex resulting from EIT. The physics allows us to determine the thermodynamic variables which describe the accompanying equilibrium state as well as the original non-equilibrium state. The explicit expression for the rate of entropy production (Section 6) identifies the dissipative mechanisms and suggests the forms of the phenomenological relations to be adopted (Section 7). In Section 8, we show that the expressions of the entropy production of the homogeneous models derived from both the two-fluid models and the mixture models are identical, contrary to the expression for the reversible entropy source terms. Finally, constitutive equations are derived from EIT considerations (Section 10), and two examples of the usefulness of their use are given in Section 11. The paper ends with some conclusions about the future of two-phase flow modelling.

2. Fluid volumes and local equilibrium

Two-phase systems can be subdivided into three main categories:

- particulate fluid flows from submicronic to large diameter particles (several millimeters),
- separated flows where the two phases are separated by a smooth or wavy interface,
- churn turbulent flows whose structure is random.

The first two categories can be subjected to detailed modelling including for example condensation and fragmentation phenomena which are typical of particulate fluid flows, wave amplitude and frequency in the case of separated flows. Particles can also be present in each phase of a separated two-phase flow due to entrainment of droplets in the gas phase or nucleate boiling in the liquid film.

To model separated flows—like annular flows—the macroscopic domain is divided into single-phase macroscopic subvolumes separated by interface surfaces. Local instantaneous equations are written for each phase separately, with jump conditions at the interfaces. At local scale (say the volume of observation of a small probe), there is only *one phase* present at a time. Averaging over time, or making ensemble averages lead to coexisting phases at any point of the domain. This is the philosophy which is behind the *two-fluid model*. The classical thermodynamic assumption of local equilibrium is easily extended to two-fluid models, since each phase is treated as a continuum: the relaxation times of the mechanical and thermal non-equilibriums of each phase are related to the mechanical and thermal diffusions at the molecular or Kolmogorov scales, and are thus very short compared with the scale at which the flow is physically observed. One can thus define and measure a temperature and a velocity for each phase at each point as a function of the measured time. A hydrodynamic and a thermodynamic pressure can also be defined for each phase as it is done for single-phase fluids.

In this paper we consider particulate flows for which mixture models can be proposed. According to the classical approach, we consider a flow volume V , which from the thermodynamic point of view is a closed system. It contains fluid particles (at least one) and a part of the surrounding continuum phase, filling a simply connected space. Due to vaporization and/or condensation, the masses m^l and m^g of the two phases are not constant, even if the total mass,

$$m = m^l + m^g, \quad (1)$$

of the flow volume is constant. The variable volume V can be subdivided into two variable subvolumes

$$V = V^l + V^g. \quad (2)$$

The two subvolumes are separated by interfacial areas which can be modelled as a third region of space including interfacial properties and energy. In this paper we neglect the surface tension and the associated surface energy and describe the state of the two-phase system in a unified manner regardless the size of the particles. This restricts the applicability of the model to particulate systems where the fluid particles have a diameter larger than 1 μm . Liquid and vapour can thus be regarded as two co-existing thermodynamic subsystems, and in this respect, they represent a weakly interacting mixture as defined by Bataille and Kestin (1979).

The situation where the time or space averaged velocities of the liquid \bar{w}_i^l and vapour \bar{w}_i^g over the volume V are different introduces the mechanical non-equilibrium. Here, we distinguish between the *non-equilibrium* state and its *accompanying equilibrium* state. The latter arises hypothetically from the former by isolating the fluid volume suddenly and maintaining the barycentric velocity constant. Then all the intensive properties (temperature, pressure, chemical potentials) and the velocities evolve towards uniformity inside the system, and its entropy increases. The original non-equilibrium state and the accompanying equilibrium state are characterized by the same global extensive variables mass, volume and internal energy. The process leading to equilibrium involves internal fluxes of mass, momentum and energy which are beyond external control, and induce coupled relaxation times.

The calculation of the entropy of the initial non-equilibrium fluid volume cannot be done without introducing the concept of local equilibrium. In the model that we propose here, the local volumes, because of their two-phase nature, are much larger than in the single-phase systems. For

example, in a bubbly flow, the smallest two-phase system consists of a vapour bubble surrounded by some volume of liquid. Irreversible processes of vaporization or condensation imply $T^l \neq T^g$, and these temperatures have to be measured at a certain distance from the interface, outside of the thermal boundary layer. As a result the relaxation times θ in two-phase systems are much larger than those in one-phase systems even of a dozen orders of magnitude. Such a long relaxation time even of 1 s was evaluated by Bilicki et al. (1990) basing on the Moby Dick experimental results by Réocreux (1974) and confirmed theoretically by Bilicki et al. (1996).

In our two-phase system we must also recognize the existence of an internal deformation variable, the mass transferred inside the system between the two phases. The chemical work expressed as the product of the chemical potential acting on the “disappearing”, as well as “appearing” masses dm^l and dm^g , must be included in the balance. In the hypothetical process of creating the accompanying equilibrium state from the non-equilibrium state an internal variable, like dm^l/m , is assumed to have been constrained by an outside agent, and the mass exchange is assumed performed reversibly at the cost of transferring work to the surroundings (De Groot and Mazur, 1962, Chapters 21 and 22).

3. Definitions

The proportions of vapour and liquid present in the closed system can be described either by the volumetric fractions

$$\phi^l = V^l/V \quad \text{and} \quad \phi^g = V^g/V \quad \text{with} \quad \phi^l + \phi^g = 1, \quad (3a)$$

or by the mass fractions

$$\gamma^l = m^l/m \quad \text{and} \quad \gamma^g = m^g/m \quad \text{with} \quad \gamma^g + \gamma^l = 1. \quad (3b)$$

In the theory of two-phase flow, volumetric fractions are preferred and

$$\phi \equiv \phi^g \quad \text{with} \quad \phi^l = 1 - \phi \quad (4)$$

is called the *void fraction*. We favour the notation of Eq. (3a) because subsequent equations acquire a more symmetric form. We shall make substitution (4) only in the working equations. It is clear that the void fraction $\phi \equiv \phi^g$ and the frequently employed *dryness fraction*

$$x \equiv \gamma^g \quad \text{with} \quad \gamma^l = 1 - x \quad (5)$$

are not independent. It is easy to show that

$$x = \frac{\phi \rho^g}{\rho^l(1 - \phi) + \rho^g \phi} \quad \text{or} \quad \phi = \frac{1}{1 + (1 - x)\rho^l/x\rho^l}. \quad (6)$$

Here

$$\rho^l = \frac{m^l}{V^l} \quad \text{and} \quad \rho^g = \frac{m^g}{V^g} \quad (7)$$

are tabulated equilibrium densities of the substance.

All extensive quantities of system V can be expressed in terms of the properties of the two co-existing subsystems. In this connection it is usual to introduce specific quantities per unit mass. In particular,

$$\rho = \phi^l \rho^l + \phi^g \rho^g, \quad (8)$$

or for any specific quantity $\psi = \Psi/m$ per unit mass

$$\rho\psi = \phi^l \rho^l \psi^l + \phi^g \rho^g \psi^g, \quad (9)$$

here ψ may be interpreted as internal energy per unit mass u , specific enthalpy h , specific entropy s , etc. As far as the non-equilibrium state is concerned, the properties ρ and ψ calculated above represent *mean values* taken over volume V . It is emphasized that the same procedure *cannot be applied to the intensive properties*. However, in the expression for the second part of the Second Law (Clausius–Duhem inequality), we have to introduce the reference temperature T_{ref} . This temperature is derived from the fundamental equation of state for the two-phase liquid vapour system (see De Groot and Mazur, 1962; Bataille and Kestin, 1975).

In the case of thermodynamic and mechanical equilibrium, the total entropy is the function

$$S = S(U, V, m^l, m^g). \quad (10)$$

In the non-equilibrium case, provided that the concept of equation of state is extended,

$$S = S(U, V, m^l, m^g, \alpha_1, \dots, \alpha_n), \quad (11)$$

and mixture temperature and mixture pressure are defined by

$$T \triangleq \left(\frac{\partial U}{\partial S} \right)_{V, m^l, m^g, \alpha_1, \dots, \alpha_n}, \quad P \triangleq - \left(\frac{\partial U}{\partial V} \right)_{S, m^l, m^g, \alpha_1, \dots, \alpha_n}.$$

The Gibbs equation can be written

$$TdS = dU + PdV - \mu^l dm^l - \mu^g dm^g + T \sum_{i=1}^n \left(\frac{\partial S}{\partial \alpha_i} \right)_{U, V, m^l, m^g, \alpha_j} d\alpha_i, \quad j \neq i. \quad (12)$$

The additional internal variables α_i are the local mass flux densities, heat flux densities, and shear stresses in the two-phase mixture.

The preceding two terms describe the reversible transfer of masses, dm^l and dm^g with

$$dm^l + dm^g = 0, \quad (13)$$

between the two subsystems, the symbols μ^l and μ^g denoting the chemical potentials of the two phases. These two quantities may or may not be equal. The Gibbs equation (12) clearly identifies the thermodynamic variables which enter the system's *equation of state*. If we approximate the system by one in which surface tension and the possible appearance of metastable states are neglected, we may equate the two chemical potentials. Then the corresponding terms cancel each other in view of Eq. (13). In the present model we shall make this simplification, but retain the last terms in our equation to preserve generality. In the absence of surface tension and metastability, pressure P is a unique function of temperature T in view of the equality of the chemical potentials of both phases.

For the accompanying equilibrium state, Gibbs equation per unit mass becomes

$$T_{\text{ref}} ds = du + Pd(1/\rho) - \mu^l d\gamma^l - \mu^g d\gamma^g, \quad (14)$$

where the mass fractions γ^l and γ^g have been introduced.

Finally it is worth noticing that the system is compressible due to the compressibility of the vapour as well as to the exchange of mass between the phases. In most cases the two phases taken separately are either practically incompressible (liquid) or compressible with very short relaxation times (saturated vapour or metastable vapour). However, the whole system exhibits a relaxation time which may become long if the rate of evaporation or condensation is not very large, or is significantly affected by surface tension. This means that the system as a whole may become the seat of viscoelastic effects which can manifest themselves in the form of non-zero bulk viscosity.

4. The present model

The model developed here corresponds to an idealised tomographic method where the fluid volume is subdivided into a large but finite number of cells, the volumetric fraction of each phase being simultaneously determined in all cells. We subdivide thus the whole system of volume V into k elements V_i . This leads to a discrete distribution of extensive (V_i, m_i^l, m_i^g, \dots), specific ($\rho_i^l, \rho_i^g, h_i^l, h_i^g, \dots$) and intensive properties ($T_i, P_i, \mu_i^l, \mu_i^g, \dots$), as well as velocities (\vec{w}_i^l, \vec{w}_i^g) throughout volume V . The *instantaneous* value of any extensive property of phase α , $\Psi^\alpha(t)$ for the whole system is equal to the sums:

$$\Psi^\alpha(t) = \sum_{i=1}^k \rho_i^\alpha \phi_i^\alpha \psi_i^\alpha V_i = \sum_{i=1}^k \gamma_i^\alpha \rho_i \psi_i^\alpha V_i. \quad (15a)$$

The instantaneous value of any extensive property $\Psi(t)$ for the whole system is equal to the sum

$$\Psi(t) = \sum_{i=1}^k \rho_i \psi_i V_i = \sum_{\alpha} \Psi^\alpha(t), \quad (15b)$$

where ρ_i and ψ_i are the instantaneous mean specific quantities introduced in Section 3.

Further, for each V_i , we assign the value of all its parameters to a particular point inside V_i , for example its centre of mass.

We now apply the Euler–McLaurin formula to Eqs. (15a) and (15b), and obtain

$$\Psi^\alpha(t) = \int_{V^l(t)} \rho^\alpha(\vec{x}, t) \phi^\alpha(\vec{x}, t) \psi^\alpha(\vec{x}, t) dV + R^\alpha, \quad (16a)$$

$$\Psi(t) = \int_{V^l(t)} \rho(\vec{x}, t) \psi(\vec{x}, t) dV + R, \quad (16b)$$

where R^α and R are the remainders.

The functions $\rho^\alpha(\vec{x}, t)$, $\phi^\alpha(\vec{x}, t)$, $\psi^\alpha(\vec{x}, t)$, $\rho(\vec{x}, t)$, and $\psi(\vec{x}, t)$ are continuous at every point \vec{x} of the transformed space $V^l(t)$, except for any subspace of measure zero (shock fronts). A necessary condition to make the remainders R^α and R negligible:

$$R^\alpha \cong 0 \quad \text{and} \quad R \cong 0$$

is to have a large number k of elements V_i , in other words

$$V_i \ll V.$$

Then one can accept the approximations:

$$\Psi^\alpha(t) \cong \int_{V^l(t)} \rho^\alpha(\vec{x}, t) \phi^\alpha(\vec{x}, t) \psi^\alpha(\vec{x}, t) dV \tag{17a}$$

and

$$\Psi(t) \cong \int_{V^l(t)} \rho(\vec{x}, t) \psi(\vec{x}, t) dV. \tag{17b}$$

Moreover, the accuracy of the void fraction distribution and of the density distribution of each phase can be checked at the scale V^l by the expressions:

$$\text{If } \psi_i^\alpha \equiv v_i, \quad \text{then } V^\alpha = \int_{V^l} \phi^\alpha(\vec{x}, t) dV \quad \text{and} \quad \sum_\alpha V^\alpha = V^l. \tag{18a}$$

$$\text{If } \psi_i^\alpha \equiv 1, \quad \text{then } m^\alpha = \int_{V^l} \rho^\alpha(\vec{x}, t) dV \quad \text{and} \quad \sum_\alpha m^\alpha = m. \tag{18b}$$

However, this is no guarantee for the uniqueness of the functions $\phi^\alpha(\vec{x}, t)$ and $\rho^\alpha(\vec{x}, t)$ at any particular point inside V^l , neither the centres of masses of the V_i s or any other points: it remains limited by the finite number of bubbles or droplets inside the fluid volume.

Another requirement for the continuous functions which are built on the initial discrete distributions, and especially for the specific values of extensive properties, is that their averages calculated over each V_i be equal to the values prescribed for V_i , by the discrete distribution:

$$\rho_i \psi_i = \frac{1}{V_i} \int_{V_i} \rho(\vec{x}, t) \psi(\vec{x}, t) dV. \tag{19}$$

Whatever the number of bubbles or drops in the fluid volume, the local volumes remain larger than those used in single-phase flow, and a fortiori the volume of a “fluid particle” on which the continuum mechanics is based.

From Eq. (18a) one can deduce an instantaneous value of the void fraction, averaged over V :

$$\phi^g = \frac{V^g}{V}.$$

This parameter differs from the void fraction used in the two-fluid model, where combined time and volume averages are used. However the ergodic theorem enables to make ensemble averages which are equivalent to time averages, and we suggest to apply this method to the quantities defined in the present model.

The continuum model of our system is similar to that introduced in the classical theory (Bataille and Kestin, 1979; Wallis, 1969), and the obvious assumption is made that the conservation laws apply. The only difference now is that we shall write separate conservation equations for the vapour and liquid in order to introduce their densities and volume fractions explicitly, which leads to the philosophy of the two-fluid model.

5. Conservation equations

In order to write down the conservation laws for the model-continuum, it is convenient to introduce the indicial notation and to adopt the Einstein summation convention. The two phases will be distinguished by l or g, as before, but to avoid repetition we shall use the superscript α to denote any one of them. No summation convention is implied with respect to the superscripts, and a summation sign will always be displayed. Thus, for example, $\gamma^\alpha w_i^\alpha$ means either $\gamma^l w_i^l$ or $\gamma^g w_i^g$, but $\sum \gamma^\alpha w_i^\alpha$ means $\gamma^l w_i^l + \gamma^g w_i^g$.

In the transformed volume $V^t(t)$ we have defined the continuous approximation functions describing the distributions of liquid and vapour velocities $w_i^l(x_k, t)$, $w_i^g(x_k, t)$, the centre-of-mass velocity $w_i(x_k, t)$, the volume fraction of liquid $\phi^l(x_k, t)$ and vapour $\phi^g(x_k, t)$, the densities of liquid $\rho^l(x_k, t)$ and vapour ρ^g , etc. In every point there are two coexisting phases with their sources of mass Γ^α , momentum M_i^α and energy E^α . Now we are in a position to constitute the model by the following set of conservation equations.

5.1. Mass balance equations

$$\frac{\partial \rho^\alpha \phi^\alpha}{\partial t} + \frac{\partial (\rho^\alpha \phi^\alpha w_i^\alpha)}{\partial x_i} = \Gamma^\alpha, \quad (20)$$

with

$$\sum_{\alpha=1}^2 \Gamma^\alpha = 0. \quad (21)$$

We introduce the material fluxes corresponding to each phase J_i^α defined as

$$J_i^\alpha = \rho^\alpha \phi^\alpha (w_i^\alpha - w_i), \quad (22)$$

satisfying equation

$$\sum_{\alpha=1}^2 J_i^\alpha = 0. \quad (23)$$

In the flux J_i^α we recognize the so called diffusive velocity

$$\tilde{w}_i^\alpha \stackrel{\text{def}}{=} w_i^\alpha - w_i, \quad (24)$$

which describes the actual velocity of the selected phase with respect to the centre-of-mass velocity w_i ,

$$w_i = \sum_{\alpha=1}^2 \gamma^\alpha w_i^\alpha = \frac{\sum_{\alpha=1}^2 \rho^\alpha \phi^\alpha w_i^\alpha}{\rho} = \frac{\sum_{\alpha=1}^2 \rho^\alpha \phi^\alpha w_i^\alpha}{\sum_{\alpha=1}^2 \rho^\alpha \phi^\alpha}. \quad (25)$$

Using the material fluxes it is possible to present the mass conservation equation (20) in another form

$$\rho \frac{d\gamma^\alpha}{dt} + \frac{\partial J_i^\alpha}{\partial x_i} = \Gamma^\alpha, \tag{26}$$

where the material derivative is taken at the velocity of the centre-of-mass.

5.2. Momentum and kinetic energy equations

The linear momentum balance equation for each phase takes the form

$$\frac{\partial \rho^\alpha \phi^\alpha w_i^\alpha}{\partial t} + \frac{\partial (\rho^\alpha \phi^\alpha w_i^\alpha w_k^\alpha)}{\partial x_k} = \rho^\alpha \phi^\alpha g_i - \frac{\partial \phi^\alpha P_{ik}^\alpha}{\partial x_k} + M_i^\alpha, \tag{27}$$

with

$$\sum_{\alpha=1}^2 M_i^\alpha = 0. \tag{28}$$

Introducing the concept that the source term can be divided into a contribution f_1 from the influx of mass Γ^α , and f_2 which is connected to the molecular and turbulent exchange of momentum between phases we are able to rewrite Eq. (27) in the following form:

$$\frac{\partial \rho^\alpha \phi^\alpha w_i^\alpha}{\partial t} + \frac{\partial (\rho^\alpha \phi^\alpha w_i^\alpha w_k^\alpha)}{\partial x_k} = \rho^\alpha \phi^\alpha g_i - \frac{\partial \phi^\alpha P_{ik}^\alpha}{\partial x_k} + \Gamma^\alpha w_i^\alpha + f_2. \tag{29}$$

The LHS of Eq. (29) can be written:

$$w_i^\alpha \left(\frac{\partial \rho^\alpha \phi^\alpha}{\partial t} + \frac{\partial \rho^\alpha \phi^\alpha w_k^\alpha}{\partial x_k} \right) + \left(\rho^\alpha \phi^\alpha \frac{\partial w_i^\alpha}{\partial t} + \rho^\alpha \phi^\alpha w_k^\alpha \frac{\partial w_i^\alpha}{\partial x_k} \right)$$

or

$$w_i^\alpha \Gamma^\alpha + \rho^\alpha \phi^\alpha \frac{dw_i^\alpha}{dt} \Big|_\alpha.$$

A special form of the momentum equation is the kinetic energy balance which comes from Eq. (29) by multiplying both sides by velocity w_i^α

$$\rho^\alpha \phi^\alpha w_i^\alpha \frac{dw_i^\alpha}{dt} \Big|_\alpha = \rho^\alpha \phi^\alpha g_i w_i^\alpha - w_i^\alpha \frac{\partial \phi^\alpha P_{ik}^\alpha}{\partial x_k} + f_2 w_i^\alpha. \tag{30}$$

5.3. Energy balance equations

The total energy balance for each phase can be presented in the following form:

$$\frac{\partial \rho^\alpha \phi^\alpha E^\alpha}{\partial t} + \frac{\partial \rho^\alpha \phi^\alpha E^\alpha w_i^\alpha}{\partial x_i} = \rho^\alpha \phi^\alpha g_i w_i^\alpha - \frac{\partial}{\partial x_i} (\phi^\alpha P_{ik}^\alpha w_k^\alpha + \phi^\alpha q_i^\alpha) + \varepsilon^\alpha, \tag{31}$$

with

$$\sum_{\alpha=1}^2 \varepsilon^{\alpha} = 0, \quad (32)$$

where

$$E^{\alpha} = u^{\alpha} + \frac{(w_i^{\alpha})^2}{2}. \quad (33)$$

We can go following the same way as we did with the momentum equation dividing the term ε^{α} into three terms namely the total energy influx due to mass transfer, the power of the viscous and turbulent forces $f_2 w_i^{\alpha}$ corresponding to momentum exchange, and the residual internal energy source $\phi^{\alpha} \rho^{\alpha} Y^{\alpha}$ due to radiation, Joule's effect, chemical or nuclear reactions, etc.

$$\frac{\partial \rho^{\alpha} \phi^{\alpha} E^{\alpha}}{\partial t} + \frac{\partial \rho^{\alpha} \phi^{\alpha} E^{\alpha} w_i^{\alpha}}{\partial x_i} = \rho^{\alpha} \phi^{\alpha} g_i w_i^{\alpha} - \frac{\partial}{\partial x_i} (\phi^{\alpha} P_{ik}^{\alpha} w_k^{\alpha} + \phi^{\alpha} q_i^{\alpha}) + \Gamma^{\alpha} \left(\frac{(w_i^{\alpha})^2}{2} + u^{\alpha} \right) + f_2 w_i^{\alpha} + \phi^{\alpha} \rho^{\alpha} Y^{\alpha}. \quad (34)$$

The LHS of Eq. (31) can be written:

$$E^{\alpha} \left(\frac{\partial \rho^{\alpha} \phi^{\alpha}}{\partial t} + \frac{\partial \rho^{\alpha} \phi^{\alpha} w_i^{\alpha}}{\partial x_i} \right) + \rho^{\alpha} \phi^{\alpha} \left(\frac{\partial E^{\alpha}}{\partial t} + w_i^{\alpha} \frac{\partial E^{\alpha}}{\partial x_i} \right)$$

or

$$E^{\alpha} \Gamma^{\alpha} + \rho^{\alpha} \phi^{\alpha} \left. \frac{dE^{\alpha}}{dt} \right|_{\alpha},$$

and Eq. (31) becomes

$$\rho^{\alpha} \phi^{\alpha} \left. \frac{dE^{\alpha}}{dt} \right|_{\alpha} = \rho^{\alpha} \phi^{\alpha} g_i w_i^{\alpha} - \frac{\partial}{\partial x_i} (\phi^{\alpha} P_{ik}^{\alpha} w_k^{\alpha} + \phi^{\alpha} q_i^{\alpha}) + f_2 w_i^{\alpha} + \phi^{\alpha} \rho^{\alpha} Y^{\alpha}. \quad (35)$$

By subtracting Eq. (30) from Eq. (35), we obtain:

$$\rho^{\alpha} \phi^{\alpha} \left. \frac{du^{\alpha}}{dt} \right|_{\alpha} = -\phi^{\alpha} P_{ij}^{\alpha} \frac{\partial w_j^{\alpha}}{\partial x_i} - \frac{\partial \phi^{\alpha} q_i^{\alpha}}{\partial x_i} + \rho^{\alpha} \phi^{\alpha} Y^{\alpha}. \quad (36)$$

5.4. Entropy balance equations

We can write the entropy balance equation for each phase

$$\frac{\partial \rho^{\alpha} \phi^{\alpha} s^{\alpha}}{\partial t} + \frac{\partial \rho^{\alpha} \phi^{\alpha} w_i^{\alpha} s^{\alpha}}{\partial x_i} = \frac{\partial J_i^{s^{\alpha}} \phi^{\alpha}}{\partial x_i} + \sigma^{\alpha} \rho^{\alpha} \phi^{\alpha}, \quad (37)$$

or in the form of the total derivative

$$\rho^{\alpha} \phi^{\alpha} \left. \frac{ds^{\alpha}}{dt} \right|_{\alpha} = \frac{\partial J_i^{s^{\alpha}} \phi^{\alpha}}{\partial x_i} + \sigma^{\alpha} \rho^{\alpha} \phi^{\alpha} - \Gamma^{\alpha} s^{\alpha}, \quad (38)$$

where the last two terms describe the sources of the entropy. One of them, $\Gamma^\alpha s^\alpha$ is reversible and connected to the mass production to the flow volume $V^\alpha(t)$ whereas another, $\sigma^\alpha \rho^\alpha \phi^\alpha$ is caused by irreversible processes and is always positive because it has to obey the second law of thermodynamics.

6. Entropy production according to classical irreversible thermodynamics (CIT)

Here we introduce the entropy equation which is a local form of the Gibbs equation. We can derive it from the equation of state of the phase α

$$s^\alpha = s^\alpha(u^\alpha, v^\alpha, \gamma^\alpha).$$

Hence, in absence of surface tension we have:

$$\left. \frac{ds^\alpha}{dt} \right|_\alpha = \left. \frac{1}{T^\alpha} \frac{du^\alpha}{dt} \right|_\alpha + \left. \frac{P}{T^\alpha} \frac{dv^\alpha}{dt} \right|_\alpha - \left. \frac{\mu^\alpha}{\gamma^\alpha T^\alpha} \frac{d\gamma^\alpha}{dt} \right|_\alpha. \tag{39}$$

This last term is unconventional in the sense that the variation of the entropy of each phase due the change of the composition of the mixture is measured at the velocity of the phase and not at the velocity of the mixture. Nevertheless, the contributions are summed up in the next step.

Multiplying (39) by $\rho^\alpha \phi^\alpha$ we can rewrite this equation in the form

$$\rho^\alpha \phi^\alpha \left. \frac{ds^\alpha}{dt} \right|_\alpha = \left. \frac{\rho^\alpha \phi^\alpha}{T^\alpha} \frac{du^\alpha}{dt} \right|_\alpha + \left. \frac{\rho^\alpha \phi^\alpha P}{T^\alpha} \frac{dv^\alpha}{dt} \right|_\alpha - \left. \frac{\mu^\alpha \rho}{T^\alpha} \frac{d\gamma^\alpha}{dt} \right|_\alpha. \tag{40}$$

Substituting $du^\alpha/dt|_\alpha$ by the RHS of Eq. (36) we get

$$\rho^\alpha \phi^\alpha \left. \frac{ds^\alpha}{dt} \right|_\alpha = - \left. \frac{\phi^\alpha P_{ij}^\alpha}{T^\alpha} \frac{\partial w_j^\alpha}{\partial x_i} - \frac{1}{T^\alpha} \frac{\partial \phi^\alpha q_i^\alpha}{\partial x_i} + \frac{1}{T^\alpha} \rho^\alpha \phi^\alpha Y^\alpha + \left. \frac{\rho^\alpha \phi^\alpha P}{T^\alpha} \frac{dv^\alpha}{dt} \right|_\alpha - \left. \frac{\mu^\alpha \rho}{T^\alpha} \frac{d\gamma^\alpha}{dt} \right|_\alpha. \tag{41}$$

Having in mind that the tensor P_{ij}^α can be subdivided into spheric and deviatoric parts

$$P_{ij}^\alpha = P \delta_{ij} + P_{ij}^{v^\alpha}, \quad P_{ij}^{v^\alpha} = P^{v^\alpha} \delta_{ij} + \widehat{P}_{ij}^{v^\alpha}, \tag{42a}$$

where

$$P^{v^\alpha} = P^{h^\alpha} - P, \tag{42b}$$

then

$$P_{ij}^\alpha = P^{h^\alpha} \delta_{ij} + \widehat{P}_{ij}^{v^\alpha}. \tag{42c}$$

we can further rearrange Eq. (41)

$$\begin{aligned} \rho^\alpha \phi^\alpha \left. \frac{ds^\alpha}{dt} \right|_\alpha = & - \frac{\phi^\alpha \widehat{P}_{ij}^{v^\alpha}}{T^\alpha} \frac{\partial w_j^\alpha}{\partial x_i} - \frac{\phi^\alpha P^{h^\alpha}}{T^\alpha} \frac{\partial w_i^\alpha}{\partial x_i} - \frac{\phi^\alpha q_i^\alpha}{(T^\alpha)^2} \frac{\partial T^\alpha}{\partial x_i} - \frac{\partial}{\partial x_i} \left(\frac{\phi^\alpha q_i^\alpha}{T^\alpha} \right) + \frac{1}{T^\alpha} \rho^\alpha \phi^\alpha Y^\alpha \\ & + \left. \frac{\rho^\alpha \phi^\alpha P}{T^\alpha} \frac{dv^\alpha}{dt} \right|_\alpha - \left. \frac{\mu^\alpha \rho}{T^\alpha} \frac{d\gamma^\alpha}{dt} \right|_\alpha. \end{aligned} \tag{43}$$

Making use of the mass balance equation (20) one obtains

$$\begin{aligned} \rho^\alpha \phi^\alpha \frac{ds^\alpha}{dt} \Big|_\alpha &= -\frac{\phi^\alpha \widehat{P}_{ij}^{v^\alpha}}{T^\alpha} \frac{\partial \widehat{w}_j^\alpha}{\partial x_i} + \frac{P^{h^\alpha} \Gamma^\alpha}{T^\alpha \rho^\alpha} - \frac{P^{h^\alpha}}{T^\alpha} \frac{d\phi^\alpha}{dt} \Big|_\alpha - \frac{\phi^\alpha q_i^\alpha}{(T^\alpha)^2} \frac{\partial T^\alpha}{\partial x_i} - \frac{\partial}{\partial x_i} \left(\frac{\phi^\alpha q_i^\alpha}{T^\alpha} \right) \\ &+ \frac{1}{T^\alpha} \rho^\alpha \phi^\alpha Y^\alpha - \frac{\mu^\alpha \rho}{T^\alpha} \frac{d\gamma^\alpha}{dt} \Big|_\alpha - \frac{\rho^\alpha \phi^\alpha (P^{h^\alpha} - P)}{T^\alpha} \frac{dv^\alpha}{dt} \Big|_\alpha. \end{aligned} \tag{44}$$

Looking at Eq. (44) through a prism of Eq. (38) it is obvious that some terms like

$$\sigma_2^\alpha = -\frac{\phi^\alpha \widehat{P}_{ij}^{v^\alpha}}{T^\alpha} \frac{\partial w_i^\alpha}{\partial x_j} \geq 0, \tag{45}$$

$$\sigma_1^\alpha = -\frac{\phi^\alpha q_i^\alpha}{(T^\alpha)^2} \frac{\partial T^\alpha}{\partial x_i} \geq 0, \tag{46}$$

$$\sigma_0^\alpha = -\frac{\phi^\alpha \rho^\alpha}{T^\alpha} (P^{h^\alpha} - P) \frac{dv^\alpha}{dt} \Big|_\alpha \geq 0, \tag{47}$$

are recognised as the entropy production terms, always positive, and $\phi^\alpha q_i^\alpha / T^\alpha$ corresponding to the entropy flux $J_i^{s^\alpha}$ both within the single phase. According to CIT $\partial w_i^\alpha / \partial x_j$ is recognised as the generalised force conjugated with the thermodynamic flux \widehat{P}_{ij} , force $\partial T^\alpha / \partial x_i$ is conjugated with flux q_i^α , and force $dv^\alpha / dt|_\alpha$ with flux $(P^{h^\alpha} - P)$ as it is well known in single-phase fluid mechanics. At the moment we cannot say anything about other terms contained in (44) except for the reversible source term $(1/T^\alpha) \rho^\alpha \phi^\alpha Y^\alpha$. Another picture appears if we consider the entropy production analysis in terms of the mixture model where there is an interaction between the phases at any point of the domain occupied by the two-phase medium. In order to do that we have to sum up the entropy equations of liquid and vapour written with respect to reference velocity of both phases, say barycentric velocity.

Starting point for this procedure is that the entropy for the two-phase mixture is expressed as

$$s = \gamma^l s^l + \gamma^g s^g$$

and the substantial derivative with respect to the barycentric velocity is:

$$\frac{ds}{dt} = \sum_\alpha \frac{d\gamma^\alpha s^\alpha}{dt} = \sum_\alpha \left[\gamma^\alpha \frac{ds^\alpha}{dt} \Big|_\alpha + s^\alpha \frac{d\gamma^\alpha}{dt} \Big|_\alpha - \tilde{w}_i^\alpha \frac{\partial \gamma^\alpha s^\alpha}{\partial x_i} \right]. \tag{48}$$

The entropy balance introduced for each phase (38) now written for both phases with respect to the barycentric velocity takes a form

$$\frac{ds}{dt} = \sum_\alpha \left[\frac{1}{\rho} \frac{\partial J_i^{s^\alpha} \phi^\alpha}{\partial x_i} + \sigma^\alpha \gamma^\alpha - \frac{\Gamma^\alpha s^\alpha}{\rho} + s^\alpha \frac{d\gamma^\alpha}{dt} \Big|_\alpha - \tilde{w}_i^\alpha \frac{\partial \gamma^\alpha s^\alpha}{\partial x_i} \right], \tag{49a}$$

$$\frac{ds}{dt} = \frac{1}{\rho} \frac{\partial J_i^{s^\alpha}}{\partial x_i} + \sigma + \psi, \tag{49b}$$

where

$$\sigma = \gamma^g \sigma^g + \gamma^l \sigma^l$$

and the reversible source of the entropy ψ is equal to

$$\psi = \sum_{\alpha} \left[-\frac{\Gamma^{\alpha} s^{\alpha}}{\rho} + s^{\alpha} \frac{d\gamma^{\alpha}}{dt} \Big|_{\alpha} - \tilde{w}_i^{\alpha} \frac{\partial \gamma^{\alpha} s^{\alpha}}{\partial x_i} \right]. \quad (49c)$$

Using Eq. (44), Eq. (48) becomes:

$$\begin{aligned} \frac{ds}{dt} = \sum_{\alpha} \left\{ -\frac{\gamma^{\alpha}}{\rho^{\alpha} T^{\alpha}} \widehat{P}_{ij}^{v^{\alpha}} \frac{\partial w_j^{\alpha}}{\partial x_i} - \frac{P^{h^{\alpha}} \Gamma^{\alpha}}{T^{\alpha} \rho^{\alpha}} + \frac{P^{h^{\alpha}}}{\rho T^{\alpha}} \frac{d\phi^{\alpha}}{dt} \Big|_{\alpha} - \frac{\gamma^{\alpha} q_i^{\alpha}}{\rho^{\alpha} (T^{\alpha})^2} \frac{\partial T^{\alpha}}{\partial x_i} - \frac{1}{\rho} \frac{\partial}{\partial x_i} \left(\frac{\phi^{\alpha} q_i^{\alpha}}{T^{\alpha}} \right) \right. \\ \left. + \frac{\gamma^{\alpha} Y^{\alpha}}{T^{\alpha}} - \left(\frac{\mu^{\alpha}}{T^{\alpha}} - s^{\alpha} \right) \frac{d\gamma^{\alpha}}{dt} \Big|_{\alpha} - \frac{\gamma^{\alpha} (P^{h^{\alpha}} - P)}{T^{\alpha}} \frac{dv^{\alpha}}{dt} \Big|_{\alpha} - \tilde{w}_i^{\alpha} \frac{\partial \gamma^{\alpha} s^{\alpha}}{\partial x_i} \right\}. \quad (50) \end{aligned}$$

Basing on the mass balance equation (20) the term before the last in the above equation can be further developed; indeed, Eq. (20) can be written:

$$\phi_{\alpha} \frac{d\rho^{\alpha}}{dt} \Big|_{\alpha} + \rho^{\alpha} \frac{d\phi^{\alpha}}{dt} \Big|_{\alpha} + \rho^{\alpha} \phi^{\alpha} \frac{\partial w_i^{\alpha}}{\partial x_i} = \Gamma^{\alpha}. \quad (51)$$

Hence,

$$\begin{aligned} -\frac{(P^{h^{\alpha}} - P)\gamma^{\alpha}}{T^{\alpha}} \frac{dv^{\alpha}}{dt} \Big|_{\alpha} &= \frac{(P^{h^{\alpha}} - P)\gamma^{\alpha}}{T^{\alpha}(\rho^{\alpha})^2} \frac{d\rho^{\alpha}}{dt} \Big|_{\alpha} \\ &= -\frac{(P^{h^{\alpha}} - P)}{T^{\alpha} \rho} \frac{d\phi^{\alpha}}{dt} - \frac{(P^{h^{\alpha}} - P)}{T^{\alpha} \rho} \tilde{w}_i^{\alpha} \frac{\partial \phi^{\alpha}}{\partial x_i} - \frac{(P^{h^{\alpha}} - P)\phi^{\alpha}}{T^{\alpha} \rho} \frac{\partial w_i^{\alpha}}{\partial x_i} + \frac{(P^{h^{\alpha}} - P)\Gamma^{\alpha}}{T^{\alpha} \rho^{\alpha}}. \quad (52) \end{aligned}$$

Then the entropy balance equation can be written

$$\begin{aligned} \frac{ds}{dt} = \sum_{\alpha} \left\{ -\frac{\gamma^{\alpha} \widehat{P}_{ij}^{v^{\alpha}}}{\rho^{\alpha} T^{\alpha}} \frac{\partial w_j^{\alpha}}{\partial x_i} - \frac{\gamma^{\alpha}}{\rho^{\alpha} T^{\alpha}} (P^{h^{\alpha}} - P) \frac{\partial w_i^{\alpha}}{\partial x_i} - \frac{P\Gamma^{\alpha}}{T^{\alpha} \rho^{\alpha}} + \frac{P}{T^{\alpha} \rho} \frac{d\phi^{\alpha}}{dt} + \frac{P}{T^{\alpha} \rho} \tilde{w}_i^{\alpha} \frac{\partial \phi^{\alpha}}{\partial x_i} \right. \\ \left. - \frac{1}{\rho} \frac{\partial}{\partial x_i} \left(\frac{\phi^{\alpha} q_i^{\alpha}}{T^{\alpha}} \right) - \frac{\gamma^{\alpha} q_i^{\alpha}}{\rho^{\alpha} (T^{\alpha})^2} \frac{\partial T^{\alpha}}{\partial x_i} + \frac{\gamma^{\alpha} Y^{\alpha}}{T^{\alpha}} - \left(\frac{\mu^{\alpha}}{T^{\alpha}} - s^{\alpha} \right) \frac{d\gamma^{\alpha}}{dt} - \frac{\mu^{\alpha}}{T^{\alpha}} \tilde{w}_i^{\alpha} \frac{\partial \gamma^{\alpha}}{\partial x_i} - \gamma^{\alpha} \tilde{w}_i^{\alpha} \frac{\partial s^{\alpha}}{\partial x_i} \right\}. \quad (53) \end{aligned}$$

It is worth noting that RHS of Eq. (53) consists of the divergence of the entropy fluxes $(1/\rho)(\partial J_i^{\alpha}/\partial x_i)$, the reversible entropy sources ψ^{α} and of the entropy production rate terms σ^{α} .

Comparing (53) with (49a)–(49c) it is easy to recognise that

$$\frac{1}{\rho} \frac{\partial J_i^{\alpha}}{\partial x_i} = -\frac{1}{\rho} \frac{\partial}{\partial x_i} \left(\frac{\phi^{\alpha} q_i^{\alpha}}{T^{\alpha}} \right), \quad (54a)$$

$$\psi^{\alpha} = -\frac{P\Gamma^{\alpha}}{T^{\alpha} \rho^{\alpha}} + s^{\alpha} \frac{d\gamma^{\alpha}}{dt} + \frac{\gamma^{\alpha} Y^{\alpha}}{T^{\alpha}} + \frac{P}{T^{\alpha} \rho} \tilde{w}_i^{\alpha} \frac{\partial \phi^{\alpha}}{\partial x_i} - \frac{\mu^{\alpha}}{T^{\alpha}} \tilde{w}_i^{\alpha} \frac{\partial \gamma^{\alpha}}{\partial x_i} - \gamma^{\alpha} \tilde{w}_i^{\alpha} \frac{\partial s^{\alpha}}{\partial x_i}, \quad (54b)$$

$$\gamma^{\alpha} \sigma^{\alpha} = -\frac{\gamma^{\alpha}}{\rho^{\alpha} T^{\alpha}} \widehat{P}_{ij}^{v^{\alpha}} \frac{\partial w_j^{\alpha}}{\partial x_i} - \frac{\gamma^{\alpha}}{\rho^{\alpha} T^{\alpha}} (P^{h^{\alpha}} - P) \frac{\partial w_i^{\alpha}}{\partial x_i} + \frac{P}{T^{\alpha} \rho} \frac{d\phi^{\alpha}}{dt} - \frac{\phi^{\alpha} q_i^{\alpha}}{\rho (T^{\alpha})^2} \frac{\partial T^{\alpha}}{\partial x_i} - \frac{\mu^{\alpha}}{T^{\alpha}} \frac{d\gamma^{\alpha}}{dt}. \quad (54c)$$

It is interesting to mention that the reversible entropy source terms Eq. (54b) in the present model originate from two different reasons. The two first terms represent a reversible transport of entropy due to phase change, i.e. evaporation or condensation. The last three terms are due to the frame change: the entropy is balanced with respect to barycentric velocity w_i instead of the local phase velocity w_i^g ; therefore, the last three terms contain the diffusive velocity. The expressions for the entropy production rate contain three parts of different tensorial rank,

$$\sigma = \sigma_2 + \sigma_1 + \sigma_0, \tag{55}$$

and satisfy the condition

$$\sigma \geq 0 \tag{56}$$

given in (45)–(47). Now for the system containing two phases exchanging mass, momentum and energy, the source terms include some additional contributions, namely

$$\sigma_2 = -\frac{\gamma^g}{\rho^g T^g} \widehat{P}_{ij}^{v^g} \frac{\partial w_i^g}{\partial x_j} - \frac{\gamma^l}{\rho^l T^l} \widehat{P}_{ij}^{v^l} \frac{\partial w_i^l}{\partial x_j} \geq 0, \tag{57a}$$

$$\sigma_1 = -\frac{\gamma^g q_i^g}{\rho^g (T^g)^2} \frac{\partial T^g}{\partial x_i} - \frac{\gamma^l q_i^l}{\rho^l (T^l)^2} \frac{\partial T^g}{\partial x_i} \geq 0, \tag{57b}$$

$$\sigma_0 = -\frac{\gamma^g}{\rho^g T^g} (P^{hg} - P) \frac{\partial w_i^g}{\partial x_i} - \frac{\gamma^l}{\rho^l T^l} (P^{hl} - P) \frac{\partial w_i^l}{\partial x_i} + \frac{P}{\rho} \frac{T^l - T^g}{T^g T^l} \frac{d\phi^g}{dt} - \left(\frac{\mu^g}{T^g} - \frac{\mu^l}{T^l} \right) \frac{d\gamma^g}{dt} \geq 0. \tag{57c}$$

7. The phenomenological assumptions

The final form of the entropy production rate contained in Eqs. (57a)–(57c) allows us to identify physically justified generalized forces and their conjugate fluxes. We make the assumption that our model-continuum is isotropic, and this means that the generalized fluxes depend only on forces of equal tensorial rank, given that the second-order tensors are traceless. The first term, σ_2 , is the scalar product of two traceless second-order tensors, the second term, σ_1 , contains scalar products of vectors, and the last term, σ_0 , contains only products of scalar quantities.

In physical terms, this denotes the absence of coupling between the forces and fluxes of the three categories, and Eq. (56) implies

$$\sigma_0 \geq 0; \quad \sigma_1 \geq 0; \quad \sigma_2 \geq 0, \tag{58}$$

separately.

Basing on CIT (Kestin, 1979), we shall assume that linear phenomenological rate-equations are justified in our case. We can represent them by the following equations:

$$\widehat{P}_{ij}^{v^g} = L_{21} \frac{1}{T^g} \frac{\partial w_i^g}{\partial x_j} + L_{22} \frac{1}{T^l} \frac{\partial w_i^l}{\partial x_j}, \tag{59a}$$

$$\widehat{P}_{ij}^{v^l} = L_{23} \frac{1}{T^g} \frac{\partial w_i^g}{\partial x_j} + L_{24} \frac{1}{T^l} \frac{\partial w_i^l}{\partial x_j}, \tag{59b}$$

$$q_i^g = L_{11} \frac{1}{T^{g^2}} \frac{\partial T^g}{\partial x_i} + L_{12} \frac{1}{T^{l^2}} \frac{\partial T^l}{\partial x_i}, \tag{59c}$$

$$q_i^l = L_{13} \frac{1}{T^{g^2}} \frac{\partial T^g}{\partial x_i} + L_{14} \frac{1}{T^{l^2}} \frac{\partial T^l}{\partial x_i}, \tag{59d}$$

$$P^{hg} - P = L_{01} \frac{1}{T^g} \frac{\partial w_i^g}{\partial x_i} + L_{02} \frac{1}{T^l} \frac{\partial w_i^l}{\partial x_i} + L_{03} \frac{T^g - T^l}{T^g T^l} + L_{04} \left(\frac{\mu^g}{T^g} - \frac{\mu^l}{T^l} \right), \tag{59e}$$

$$P^{hl} - P = L_{05} \frac{1}{T^g} \frac{\partial w_i^g}{\partial x_i} + L_{06} \frac{1}{T^l} \frac{\partial w_i^l}{\partial x_i} + L_{07} \frac{T^g - T^l}{T^g T^l} + L_{08} \left(\frac{\mu^g}{T^g} - \frac{\mu^l}{T^l} \right), \tag{59f}$$

$$\frac{d\phi^g}{dt} = L_{09} \frac{1}{T^g} \frac{\partial w_i^g}{\partial x_i} + L_{010} \frac{1}{T^l} \frac{\partial w_i^l}{\partial x_i} + L_{011} \frac{T^g - T^l}{T^g T^l} + L_{012} \left(\frac{\mu^g}{T^g} - \frac{\mu^l}{T^l} \right), \tag{59g}$$

$$\frac{d\gamma^g}{dt} = L_{013} \frac{1}{T^g} \frac{\partial w_i^g}{\partial x_i} + L_{014} \frac{1}{T^l} \frac{\partial w_i^l}{\partial x_i} + L_{015} \frac{T^g - T^l}{T^g T^l} + L_{016} \left(\frac{\mu^g}{T^g} - \frac{\mu^l}{T^l} \right). \tag{59h}$$

The forces in Eqs. (59a) and (59b) are odd and in Eqs. (59c)–(59f) are even, and for this reason the Onsager–Casimir reciprocal relations impose the conditions

$$L_{22} = L_{23}, \quad L_{12} = L_{13}, \tag{60a, b}$$

and

$$L_{02} = L_{05}, \quad L_{03} = L_{09}, \quad L_{04} = L_{013}, \quad L_{07} = L_{010}, \quad L_{08} = L_{014}, \quad L_{012} = L_{015}. \tag{61a–f}$$

Some phenomenological coefficients have a well known interpretation for example an expression of the thermal conductivity, $L_{13} \approx -\lambda^g T^{g^2}$, an expression of the viscosity, $L_{22} \approx -\eta T^l$, or an expression of the bulk viscosity, $L_{01} \approx -\zeta T^g$, etc. What might be surprising for a reader is that the constitutive equations describing the generalised thermodynamic fluxes for a separate phase depend on the conjugate forces for both phases. This should be considered as a consequence of the nature of the two-fluid model which consists in that in any point of the continuum domain there are two separate phases.

8. Simplified form: the homogeneous models

Homogeneous models derived from the two-fluid model (HTFM) as well as from the mixture model (HMM) can be simplified. According to the assumptions made, we can consider the homogeneous non-equilibrium two-fluid model (HNETFM) or the homogeneous equilibrium two-fluid model (HETFM) on the one hand, and the homogeneous non-equilibrium mixture model (HNEMM) or the homogeneous equilibrium mixture model (HEMM) on the other hand.

In a drastically simplified version of the two-fluid model (HTFM) (equilibrium or not), we can neglect the phase slip resulting in that

$$w_i^g = w_i^l = w_i, \tag{62}$$

and consequently

$$\tilde{w}_i^\alpha = 0. \tag{63}$$

Another assumption is that we base on the reference temperature T_{ref} introduced in Section 3, instead of setting two different temperatures of the liquid and vapour in the Gibbs equation.

Further, we assume:

$$P^{hg} = P^{hl} = P^h, \quad (64)$$

and we define:

$$\tilde{P}_{ij}^v = \phi^g \tilde{P}_{ij}^{vg} + \phi^l \tilde{P}_{ij}^{vl}, \quad (65)$$

$$q_i = \phi^g q_i^g + \phi^l q_i^l, \quad (66)$$

$$Y = \gamma^g Y^g + \gamma^l Y^l. \quad (67)$$

This set of assumptions constitute the homogeneous two-fluid model (HTFM) of the two-phase system. HTFM is different from HMM as we will see further on.

Then the entropy balance equation (53) is reduced to the not surprising equation:

$$\frac{ds}{dt} = (s^g - s^l) \frac{d\gamma^g}{dt} - \frac{1}{\rho} \frac{\partial q_i}{\partial x_i} - \frac{P_{ij}^v}{\rho T_{\text{ref}}} \frac{\partial w_i}{\partial x_j} - \frac{q_i}{\rho T_{\text{ref}}^2} \frac{\partial T_{\text{ref}}}{\partial x_i} - \frac{1}{T_{\text{ref}}} (\mu^g - \mu^l) \frac{d\gamma^g}{dt} + \frac{Y}{T_{\text{ref}}}. \quad (68a)$$

The above equation can be expressed in terms of the entropy flux J_i^s , the entropy production rate σ and the reversible entropy source ψ

$$\frac{ds}{dt} = -\frac{1}{\rho} \frac{\partial J_i^s}{\partial x_i} + \sigma + \psi, \quad (68b)$$

where

$$\psi = (s^g - s^l) \frac{d\gamma^g}{dt} + \frac{Y}{T_{\text{ref}}}, \quad (68c)$$

$$J_i^s = \frac{q_i}{T_{\text{ref}}}, \quad (68d)$$

and

$$\sigma = -\frac{\widehat{P}_{ij}^v}{\rho T_{\text{ref}}} \frac{\partial w_i}{\partial x_j} - \frac{q_i}{\rho T_{\text{ref}}^2} \frac{\partial T}{\partial x_i} - \frac{1}{T_{\text{ref}}} (\mu^g - \mu^l) \frac{d\gamma^g}{dt} - \frac{1}{\rho T_{\text{ref}}} (P^h - P) \frac{\partial w_i}{\partial x_i}. \quad (68e)$$

As mentioned above, the two-fluid model is not reduced to the homogeneous mixture model even if the simplifications (62)–(67), that are valid for HMM, are introduced. The reason is the fundamental assumption for the two-fluid model consisting on that in any point of the two-phase domain there are two separate phases of liquid and vapour. In the case of HMM that condition is not satisfied because one assumes coexisting two phases in any point of the field satisfying the equation of state described by the specific entropy $s = s^l \gamma^l + s^g \gamma^g$, the specific internal energy $u = u^l \gamma^l + u^g \gamma^g$, the specific volume $v = v^l \gamma^l + v^g \gamma^g$ and the dryness fraction $\gamma = \gamma^g$. The equation of state is expressed as

$$s = s(u, v, \gamma). \quad (69)$$

Equations of mass, momentum and energy balance describing HMM take a specific form of equations (20), (27) and (36) corresponding to the mixture of two-phases in any point of the system. These equations look like those describing a single phase system, namely, mass balance

$$\frac{d\rho}{dt} + \rho \frac{\partial w_i}{\partial x_i} = 0, \quad (70a)$$

or

$$\rho \frac{dv}{dt} + \frac{\partial w_i}{\partial x_i} = 0, \quad (70b)$$

momentum balance

$$\rho \frac{dw_i}{dt} = g_i - \frac{\partial P_{ik}}{\partial x_k}, \quad (71)$$

and energy balance

$$\rho \frac{du}{dt} = -P_{ik} \frac{\partial w_i}{\partial x_k} - \frac{\partial q_i}{\partial x_i} + \rho Y. \quad (72)$$

The Gibbs equation for the two-phase homogeneous system reads

$$T_{\text{ref}} \frac{ds}{dt} = \frac{du}{dt} + P \frac{dv}{dt} - (\mu^g - \mu^l) \frac{d\gamma}{dt}. \quad (73)$$

Substituting du/dt from (72), dv/dt from (70b) and making use of expressions (42a)–(42c) we can rewrite (73) into a form well known in the CIT:

$$\rho T_{\text{ref}} \frac{ds}{dt} = -\widehat{P}_{ik}^v \frac{\partial w_i}{\partial x_k} + (P - P^h) \frac{\partial w_i}{\partial x_i} - \frac{\partial q_i}{\partial x_i} - (\mu^g - \mu^l) \frac{d\gamma}{dt} + \rho Y. \quad (74)$$

Eq. (74) is different Eq. (68a) because it does not contain a term responsible for the reversible source of the entropy $(s^g - s^l)(d\gamma^g/dt)$. The interesting thing is that the entropy production rate for the HMM is identical as for the HTFM described by (68e). Consequently to that the constitutive equations derived from CIT for both HMM and HTFM are the same.

9. Extended irreversible thermodynamics (EIT) for a two-phase system

Similarly to CIT, the EIT can also be applied to describe two-phase systems. For the simplicity we confine our analysis to HMM. The analysis starts with the postulate of the extended form of the state equation, compared to Eq. (69), namely

$$s = s(u, v, \gamma^g, P^v, q_i, \widehat{P}_{ij}^v, \dot{\gamma}^g), \quad (75)$$

where $\dot{\gamma}^g = d\gamma^g/dt$. Eq. (75) contains the generalised thermodynamic fluxes coming from CIT which give rise to additional entropy productions due to phase change processes. Proceeding further with the lines of the algorithm developed earlier for single-phase systems, let us write the Gibbs equation in an extended form

$$\begin{aligned} ds &= \left(\frac{\partial s}{\partial u} \right)_{a_1} du + \left(\frac{\partial s}{\partial v} \right)_{b_1} dv + \left(\frac{\partial s}{\partial \mathbf{q}} \right)_{c_1} \cdot d\mathbf{q} + \left(\frac{\partial s}{\partial P^v} \right)_{d_1} dP^v + \left(\frac{\partial s}{\partial \gamma^g} \right)_{e_1} d\gamma^g + \left(\frac{\partial s}{\partial \widehat{\mathbf{P}}^v} \right)_{f_1} \\ &: d\widehat{\mathbf{P}}^v + \left(\frac{\partial s}{\partial \dot{\gamma}^g} \right)_{g_1} d\dot{\gamma}^g. \end{aligned} \quad (76)$$

Then, by analogy to the single-phase system, definitions of the partial derivatives can be found

$$\left(\frac{\partial s}{\partial u} \right)_{a_1=u,v,\gamma^g,q,P^v,\widehat{\mathbf{P}}^v,\dot{\gamma}^g} \triangleq T^{-1}(u, v, \gamma^g, q, P^v, \widehat{\mathbf{P}}^v, \dot{\gamma}^g), \quad (77)$$

$$\left(\frac{\partial s}{\partial v} \right)_{b_1=u,\gamma^g,q,P^v,\widehat{\mathbf{P}}^v,\dot{\gamma}^g} \triangleq T^{-1}P(u, v, \gamma^g, q, P^v, \widehat{\mathbf{P}}^v, \dot{\gamma}^g), \quad (78)$$

$$\left(\frac{\partial s}{\partial \mathbf{q}} \right)_{c_1=u,v,\gamma^g,P^v,\widehat{\mathbf{P}}^v,\dot{\gamma}^g} \triangleq T^{-1}v\alpha_1(u, v, \gamma^g, q, P^v, \widehat{\mathbf{P}}^v, \dot{\gamma}^g), \quad (79)$$

$$\left(\frac{\partial s}{\partial P^v} \right)_{d_1=u,v,\gamma^g,q,\widehat{\mathbf{P}}^v,\dot{\gamma}^g} \triangleq -T^{-1}v\alpha_{01}(u, v, \gamma, q, P^v, \widehat{\mathbf{P}}^v, \dot{\gamma}^g), \quad (80)$$

$$\left(\frac{\partial s}{\partial \gamma^g} \right)_{e_1=u,v,q,P^v,\widehat{\mathbf{P}}^v,\dot{\gamma}^g} \triangleq -T^{-1}v\alpha_{02}(u, v, \gamma, q, P^v, \widehat{\mathbf{P}}^v, \dot{\gamma}^g), \quad (81)$$

$$\left(\frac{\partial s}{\partial \widehat{\mathbf{P}}^v} \right)_{f_1=u,v,\gamma^g,q,P^v,\dot{\gamma}^g} \triangleq -T^{-1}v\widehat{\alpha}_2(u, v, \gamma^g, q, P^v, \widehat{\mathbf{P}}^v, \dot{\gamma}^g), \quad (82)$$

$$\left(\frac{\partial s}{\partial \dot{\gamma}^g} \right)_{g_1=u,v,\gamma^g,q,P^v,\widehat{\mathbf{P}}^v} \triangleq -T^{-1}v\alpha_{03}(u, v, \gamma^g, q, P^v, \widehat{\mathbf{P}}^v, \dot{\gamma}^g). \quad (83)$$

The above definitions contain quantities α_1 , α_{0i} and $\widehat{\alpha}_2$ of a vectorial, scalar and tensorial character, respectively. These quantities can have very complex forms. Assuming the most simple linear form for these coefficients,

$$\alpha_1 = \alpha_{10}\mathbf{q}, \quad \widehat{\alpha}_2 = \alpha_{21}\widehat{\mathbf{P}}^v, \quad \alpha_{01} = \alpha_{001}P^v \quad \text{and} \quad \alpha_{03} = \alpha_{002}\dot{\gamma}^g, \quad (84)$$

and placing them into Eq. (76), then taking into account conservation equation for HMM, the generalised Gibbs equation can be obtained

$$\begin{aligned} \dot{s} &= -T^{-1}\nabla \cdot \mathbf{q} - T^{-1}P^v\nabla \cdot \mathbf{w} - T^{-1}(\mu^g - \mu^l)\dot{\gamma}^g - T^{-1}\widehat{\mathbf{P}}^v : \widehat{\mathbf{V}} \\ &- T^{-1}\alpha_{001}P^v\dot{P}^v - T^{-1}\alpha_{10}\mathbf{q} \cdot \dot{\mathbf{q}} - T^{-1}\alpha_{21}\widehat{\mathbf{P}}^v : (\widehat{\mathbf{P}}^v) \cdot - T^{-1}\alpha_{002}\dot{\gamma}^g \frac{d\dot{\gamma}^g}{dt}. \end{aligned} \quad (85)$$

The entropy flux for the two-phase medium is assumed by several terms including one connected with the phase change,

$$\mathbf{J}^s = T^{-1}\mathbf{q} + \beta_{01}P^v\mathbf{q} + \beta_{10}\widehat{\mathbf{P}}^v \cdot \mathbf{q} + \beta_{02}\dot{\gamma}^g\mathbf{q} \quad (86)$$

where coefficients β are functions of u , v , γ^g

$$\beta = \beta(u, v, \gamma^g). \quad (87)$$

Placing the expression with the entropy flux divergences ($\partial J_i^s / \partial x_i$) into Eq. (85), the entropy production sources can be rewritten as

$$\begin{aligned} \sigma = & \mathbf{q} \cdot (\nabla T^{-1} - T^{-1} \alpha_{10} \dot{\mathbf{q}} + \beta_{10} \nabla \cdot \widehat{\mathbf{P}}^v + \beta_{01} \nabla P^v + \varepsilon_1 P^v \nabla \beta_{01} + \varepsilon_2 \widehat{\mathbf{P}}^v \cdot \nabla \beta_{10} + \beta_{02} \nabla \dot{\gamma}^g + \varepsilon_3 \dot{\gamma}^g \nabla \beta_{02}) \\ & + P^v \left[-T^{-1} \nabla \cdot \mathbf{w} - T^{-1} \alpha_{001} \dot{P}^v + (1 - \varepsilon_1) \mathbf{q} \cdot \nabla \beta_{01} + \beta_{01} \nabla \cdot \mathbf{q} \right] \\ & + \dot{\gamma}^g \left[-T^{-1} (\mu^g - \mu^l) - T^{-1} \alpha_{002} \frac{d\dot{\gamma}^g}{dt} + \beta_{02} \nabla \cdot \mathbf{q} + (1 - \varepsilon_3) \mathbf{q} \cdot \nabla \beta_{02} \right] \\ & + \widehat{\mathbf{P}}^v \cdot \left[-T^{-1} \widehat{\mathbf{V}} - T^{-1} \alpha_{21} (\widehat{\mathbf{P}}^v)^\cdot + \beta_{10} (\widehat{\nabla} \mathbf{q})^s + (1 - \varepsilon_2) (\mathbf{q} \widehat{\nabla} \beta_{10})^s \right]. \end{aligned} \quad (88)$$

Assuming that the coefficients β are constant and introducing coefficients φ to calibrate the evolution equations to the laws of physics, in particular the second law of thermodynamics, and making use of the Curie principle on cross effects for scalar fluxes P^v and $\dot{\gamma}^g$, and introducing further simplification (see Bilicki, 2001) the evolution equations describing the generalised thermodynamic fluxes can be presented in the form

$$\nabla T^{-1} - T^{-1} \alpha_{10} \dot{\mathbf{q}} = \varphi_{10} \mathbf{q}, \quad (89)$$

$$-T^{-1} \chi_1 (\mu^g - \mu^l) - T^{-1} \nabla \cdot \mathbf{w} - T^{-1} \alpha_{001} \dot{P}^v = \varphi_{01} P^v, \quad (90)$$

$$T^{-1} \chi_2 \nabla \cdot \mathbf{w} - T^{-1} (\mu^g - \mu^l) - T^{-1} \alpha_{002} \frac{d\dot{\gamma}^g}{dt} = \varphi_{001} \dot{\gamma}^g, \quad (91)$$

$$-T^{-1} \widehat{\mathbf{V}} - T^{-1} \alpha_{21} (\widehat{\mathbf{P}}^v)^\cdot = \varphi_{21} \widehat{\mathbf{P}}^v. \quad (92)$$

Among these constitutive equations the most interesting is Eq. (91) providing the gradient of the dryness fraction $\dot{\gamma}^g = d\gamma^g/dt$ and the second derivatives of γ^g with respect time and space.

10. Examples of application

10.1. Rapid depressurisation

The application of CIT or EIT to model a given two-phase system needs the introduction some appropriate approximations or even transformations of the constitutive equations (59a)–(59f) or (89)–(92), respectively. As a first example we have selected an interesting phenomenon occurring during a rapid depressurisation of cold water at temperature of 21 °C from 80 bar to the atmospheric pressure. The data we use come from the experiments carried out by Lienhard's group (Borkar et al., 1977).

The description of rapid depressurisation becomes complex when both phase change and pressure difference $P^v \neq 0$ (Eq. (42b)) are taken into consideration. In this case, both irreversible processes leading to generalised fluxes $\dot{\gamma}$ and P^v are, in accordance with the Curie principles (Kestin, 1979), mutually coupled, because the thermodynamic incentives giving rise to these fluxes are both

zero-rank tensors as it is shown in Section 7. Moreover it seems reasonable to restrict the modelling to 1D, and to homogeneous model. Then, with the CIT approach, we have to combine equations (59e) and (59f) into one constitutive equation for the mixture Eq. (93b). We further assume that $L_{03} = L_{07} = 0$. In Eq. (59f) we also combine the first two terms, and we assume $L_{015} = 0$. This leads to Eq. (93a). Therefore, both processes are described by the following coupled equations

$$\frac{d\gamma}{dt} = L_{11}(\mu^l - \mu^g) + L_{12} \frac{\partial w_i}{\partial z_i}, \quad (93a)$$

$$P^v = L_{21}(\mu^l - \mu^g) + L_{22} \frac{\partial w_i}{\partial z_i}, \quad (93b)$$

or, if the postulates of EIT for P^v are taken into account, Eq. (90) becomes Eq. (94b):

$$\frac{d\gamma}{dt} = L_{11}(\mu^l - \mu^g) + L_{12} \frac{\partial w_i}{\partial z_i}, \quad (94a)$$

$$\theta_P \frac{dP^v}{dt} + P^v = L_{21}(\mu^l - \mu^g) + L_{22} \frac{\partial w_i}{\partial z_i}. \quad (94b)$$

Eqs. (94a) and (94b) appear to form a more legitimate description of the process than Eqs. (93a) and (93b) by virtue of their evolutionary character. Indeed, only the first equation from Eqs. (93a) and (93b) possesses the evolutionary character, thus describing the history of the dryness fraction since the inception of the phase change process, the other equation not attempting to account for the dynamics of the process.

The theory presented here was compared with experimental results obtained by Borkar et al. (1977). In the experiment, a depressurisation of cold water during outflow from a pressurised channel was observed. In the present calculation, the 1D HMM was used:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho w)}{\partial z} = -\frac{\rho w}{A} \frac{dA}{dz}, \quad (95)$$

$$\rho \frac{dw}{dt} = -\frac{\partial P^h}{\partial z} + \frac{\partial}{\partial z} \left[\frac{4}{3} \eta \frac{dw}{dz} \right] - \tau_w \frac{C}{A}, \quad (96)$$

$$\rho \frac{dh}{dt} - \frac{dP}{dt} = \tau_w w \frac{C}{A} + (P - P^h) \frac{\partial w}{\partial z} + \left(\frac{4}{3} \eta \right) \left(\frac{dw}{dz} \right)^2 + \frac{\partial}{\partial z} \left(\lambda \frac{\partial T_S}{\partial z} \right), \quad (97)$$

where T_S is the saturation temperature, A the cross sectional area of the channel, C its perimeter, $\tau_w = \frac{1}{2} f \rho w^2 / 2$ the shear stress at the wall, f the Fanning friction factor, λ and η are the operative thermal conductivity and viscosity respectively. These last parameters have been introduced in Bilicki et al. (1996) and Kwidzinski and Bilicki (1998). The above equations are supplemented with the evolution equations (94a) and (94b) after certain modifications. Namely, it is assumed that the measure of the non-equilibrium expressed in Eq. (94a) by a difference of the chemical potentials, $\mu^l - \mu^g$, may be substituted by the difference of actual and equilibrium dryness fractions, $\gamma - \bar{\gamma}$. Moreover, it is assumed that $L_{11} = -1/\gamma$, $L_{21} = 0$ and $L_{12} = L_{22} = \zeta$ where θ_γ is a relaxation time for the evolution of dryness fraction and ζ is the bulk viscosity. The calculations of the rapid depressurisation were performed with the following values for the model parameters:

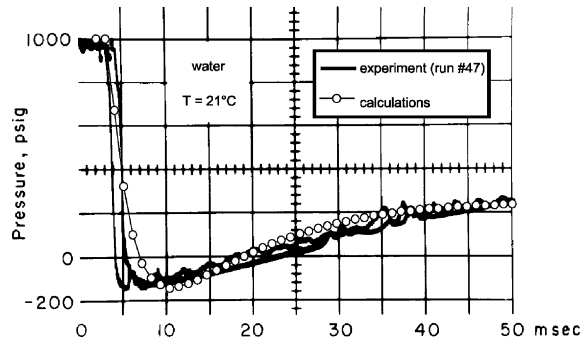


Fig. 1. Comparison of pressure profiles observed in Lienhard's experiment (Borkar et al., 1977) and calculated with the present theory.

$f = 0.008$, $\lambda = 5 \text{ W/m K}$, $\eta = 0.1 \text{ kg/m s}$, $\theta_\gamma = 10^{-2} \text{ s}$, $\theta_p = 10^{-4} \text{ s}$. The results illustrated in Fig. 1 show a good agreement between the proposed theory and the experiments.

10.2. Wall shear stress in transient single- and two-phase flows

A second example is proposed in Kucienska et al. (submitted for publication). The experiments were made for the flow of air in a tube at the atmospheric pressure. The tube has a length of 1.13 m and an internal diameter $D = 32 \text{ mm}$. The initial mass flow rate is 0.04 kg s^{-1} . Water hammer is caused by the fast closure of a valve at the downstream end of the pipe. According to EIT, the state equation is given by:

$$s = s(u, \rho, \bar{\tau}), \quad (98)$$

where $\bar{\tau}$ is the wall shear stress introduced here as a 1D dissipative flux. Its constitutive equation is found to be:

$$\bar{\tau} = f \frac{\rho w \vec{w}}{2} + f \frac{\rho^2 w D T}{4} \frac{\partial s}{\partial \tau^2} \frac{d\bar{\tau}}{dt} = \bar{\tau}_s - \theta \frac{d\bar{\tau}}{dt}. \quad (99)$$

Eq. (99) is a 1D approximation of Eq. (92). It is shown that Eq. (99) can be transformed into

$$\bar{\tau} = f \frac{\rho w \vec{w}}{2} + \frac{k \rho D}{4} \frac{d\vec{w}}{dt}, \quad (100)$$

where k a negative constant. The effect of the second term of the RHS. is to increase the friction during the deceleration and to decrease it during acceleration, but the effect of the additional friction term during deceleration is much greater than during acceleration which results in overall greater friction over the whole period of the transient than in steady state. A comparison between this model and the experiment is shown in Fig. 2.

The application of Eq. (99) for two-phase flow shows that the unsteady friction model based on EIT gives more pressure damping and a slight negative shear stress in comparison with similar calculations made with the steady-state shear stress model. Flashing occurs when the pressure wave comes back to the valve. Due to the smaller pressure amplitude, the void fraction obtained with the unsteady friction model is significantly smaller than with the steady one.

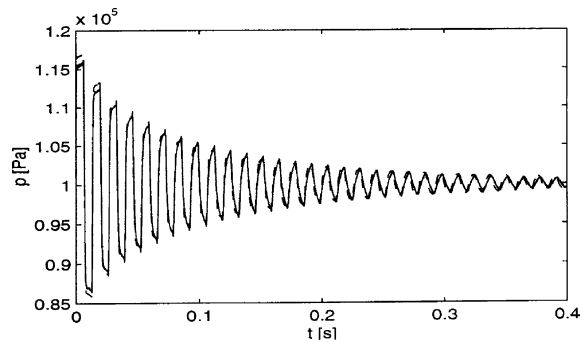


Fig. 2. Air flow, pressure versus time. Comparison between unsteady friction model derived from EIT (dashed line) and experimental results (solid line) at the valve; $k = -0.05$ for deceleration, and $k = 0$ for acceleration.

11. Conclusions

As expected, the system of equations describing a two-phase system, though complicated, is a closed one. At least in principle, it is possible to determine all dependent field variables as functions of position and time by solving the full set of partial differential equations, subject to the approximate boundary and initial conditions. It is possible to derive the constitutive equations if we rely on the philosophy and methods based on the Thermodynamics of Irreversible Processes, both classical (CIT) or extended (EIT). It is worth noting that EIT applied here offers the description of an evolution of the dryness fraction of the two-phase system which depends on a second derivatives with respect time and space.

The phenomenological coefficients $L_{\alpha\beta}$ introduced in Eqs. (59)–(61) and α , φ , χ in Eqs. (89)–(92) represent unknown quantities, because all past experimentation has been carried out in terms of more heuristic theories. Consequently, at this stage, nothing can be said about them, except that their values, all functions of the thermodynamic parameters of the state, must vary from flow pattern to flow pattern. Strictly speaking, they must vary even for a class of flows characterised by the same topological configuration, except that here we may expect that a suitably conceived ensemble averaging will provide us with an adequate approximation.

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