

**A MODEL FOR THE TRANSITION  
BETWEEN INCOMPRESSIBLE PHASES**

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**Abstract:** The purpose of the paper is to set up a model for the non-isothermal transition between incompressible phases. The scheme involves an order parameter as a phase field. Because of the incompressibility the phase field is identified with the volume fraction occupied by one of the phases. As a whole, the phases are regarded as a reacting mixture. The paper develops the analysis of the thermodynamic restrictions and provides a set of relations for the constitutive equations. The free energy is shown to play the role of a potential which provides the entropy and enters the diffusion flux and the mass growth of the transition. This in turn determines the evolution equation for the phase field. As an application, Clapeyron's equation is shown to follow for the temperature-pressure relation at equilibrium between the phases.

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## 1. Introduction

Phase transition phenomena are most often described by one of two models, the sharp interface and the diffuse interface. In a sharp interface, pure phases are separated by a moving surface thus resulting in a moving boundary problem. Within the phases, appropriate partial differential equations hold and they are solved subject to boundary conditions on the interface across which certain fields may suffer jump discontinuities.

In a diffuse interface, the individual phases (e.g. solid and liquid) are distinguished by pertinent fields (e.g. mass densities) and one or more so-called phase fields which complete the description of the body in the diffuse interface region  $\Omega$ . The phase fields are also called order parameters. Along with all other pertinent fields, they do not jump, across any surface, but change smoothly within  $\Omega$ . Phase field models are widely applied in the literature about phase transitions (see Boettinger et al [2], Chen [5]).

The purpose of this paper is to set up a model for the transition between incompressible phases. This scheme is appropriate in many circumstances, in particular for the ice-water transition. The phase field is identified with the volume fraction occupied by one of the phases and the diffuse interface is regarded to consist of a reacting mixture of incompressible constituents. This view of the diffuse interface is considered, e.g., by Müller [12], Morro [10]. More often the view adopted is that of a single body with a phase field and an internal structure described by microforces (see Gurtin [8], Frémond [7]).

The model is non-isothermal in that the temperature is allowed to vary in time and space. The main result of the paper is the analysis of the thermodynamic restrictions and a set of relations for the constitutive equations. The free energy plays the role of a potential which provides the entropy and enters the diffusion flux and the mass growth of the transition. This in turn determines the evolution equation for the phase field. As an application, Clapeyron's equation is shown to follow for the temperature-pressure relation at equilibrium between the phases.

**Notation.** We denote by  $\mathbf{x} \in \Omega \subseteq \mathbb{R}^3$  a position vector. Cartesian coordinates  $x_1, x_2, x_3$  are used and  $\partial_p$  denotes partial differentiation with respect to  $x_p$ ,  $p = 1, 2, 3$ . Also,  $t \in \mathbb{R}$  is the time and  $\partial_t$  is the partial time differentiation. We denote by  $\nabla$  and  $\nabla \cdot$  the gradient and the divergence. Moreover,  $\mathbf{u} \cdot \mathbf{v}$  is the inner product between the vectors  $\mathbf{u}, \mathbf{v}$ ,  $\text{sym}$  denotes the symmetric part and  $\text{Sym}$  is the space of symmetric tensors. Also  $\text{tr}$  is the trace whereas a superposed  $\circ$  denotes the traceless part of a tensor.

## 2. Mixtures of Incompressible Phases

The region  $\Omega$  is occupied by a mixture of  $n$  phases. Denote by the subscripts  $\alpha, \beta = 1, 2, \dots, n$  the quantities pertaining to the phases. Hence  $\rho_\alpha$  is the mass density and  $\mathbf{v}_\alpha$  is the velocity of the  $\alpha$ -th phase. For any function  $\phi_\alpha(\mathbf{x}, t)$ , on  $\Omega \times \mathbb{R}$ , a backward prime denotes the total time derivative associated with the

motion of phase  $\alpha$ , namely

$$\dot{\phi}_\alpha := \partial_t \phi_\alpha + \mathbf{v}_\alpha \cdot \nabla \phi_\alpha.$$

As with any reacting mixture, the mass density  $\rho_\alpha$  satisfies the continuity equation

$$\dot{\rho}_\alpha = -\rho_\alpha \nabla \cdot \mathbf{v}_\alpha + \tau_\alpha, \quad \alpha = 1, \dots, n,$$

where  $\tau_\alpha$  is the mass growth that is the mass production per unit volume and unit time. Equivalently, we can write

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha) = \tau_\alpha, \quad \alpha = 1, \dots, n. \quad (1)$$

The mass conservation implies that

$$\sum_\alpha \tau_\alpha = 0. \quad (2)$$

The mass density  $\rho$  and the velocity  $\mathbf{v}$  of the mixture, regarded as a single body, are defined by

$$\rho = \sum_\alpha \rho_\alpha, \quad \mathbf{v} = \frac{1}{\rho} \sum_\alpha \rho_\alpha \mathbf{v}_\alpha.$$

Accordingly, summation of (1) over  $\alpha$  and account of (2) give

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (3)$$

Let

$$c_\alpha := \frac{\rho_\alpha}{\rho}, \quad \mathbf{u}_\alpha := \mathbf{v}_\alpha - \mathbf{v}.$$

Hence  $c_\alpha$  and  $\mathbf{v}_\alpha$  are the concentration and the relative (or diffusion) velocity of phase  $\alpha$ . Let a superposed dot denote the time derivative following the mean motion, with velocity  $\mathbf{v}$ , namely

$$\dot{\phi} = \partial_t \phi + \mathbf{v} \cdot \nabla \phi.$$

Equation (1), in the form

$$\partial_t (\rho c_\alpha) + \nabla \cdot [\rho_\alpha (\mathbf{v} + \mathbf{u}_\alpha)] = \tau_\alpha, \quad (4)$$

and the observation that

$$\rho \partial_t c_\alpha + \rho (\mathbf{v} \cdot \nabla) c_\alpha = \rho \dot{c}_\alpha$$

provide

$$\rho \dot{c}_\alpha = -\nabla \cdot \mathbf{j}_\alpha + \tau_\alpha, \quad \alpha = 1, \dots, n, \quad (5)$$

where

$$\mathbf{j}_\alpha := \rho_\alpha \mathbf{u}_\alpha \quad (6)$$

is the diffusion flux of phase  $\alpha$ . It follows from the definition (6) that

$$\sum_\alpha \mathbf{j}_\alpha = 0. \quad (7)$$

Moreover, it follows from (3) that

$$\dot{\rho} = -\rho \nabla \cdot \mathbf{v}. \quad (8)$$

Also, by (1) we have

$$\dot{\rho}_\alpha + \rho_\alpha \nabla \cdot \mathbf{v} = -\nabla \cdot \mathbf{j}_\alpha + \tau_\alpha,$$

whence, by (8),

$$\dot{\rho}_\alpha - c_\alpha \dot{\rho} = -\nabla \cdot \mathbf{j}_\alpha + \tau_\alpha. \quad (9)$$

So far everything is true for any mixture of compressible phases (or constituents). Henceforth we let the phases be incompressible. This means that any phase  $\alpha$  has a constant true density, say  $\bar{\rho}_\alpha$ , that is the mass, per unit volume, in a region occupied by phase  $\alpha$  only. Denote by  $\varphi_\alpha$ , on  $\Omega \times \mathbb{R}$ , the volume fraction occupied by phase  $\alpha$  (see Bowen [3]),

$$\sum_\alpha \varphi_\alpha = 1. \quad (10)$$

Hence

$$\rho_\alpha = \bar{\rho}_\alpha \varphi_\alpha, \quad \alpha = 1, \dots, n,$$

and

$$\rho = \sum_\beta \bar{\rho}_\beta \varphi_\beta.$$

Substitution in (9) yields

$$\bar{\rho}_\alpha \dot{\varphi}_\alpha - c_\alpha \sum_\beta \bar{\rho}_\beta \dot{\varphi}_\beta = -\nabla \cdot \mathbf{j}_\alpha + \tau_\alpha, \quad \alpha = 1, \dots, n, \quad (11)$$

the concentration  $c_\alpha$  being determined by the volume fractions  $\{\varphi_\beta\}$  through the relation

$$c_\alpha = \frac{\bar{\rho}_\alpha \varphi_\alpha}{\sum_\beta \bar{\rho}_\beta \varphi_\beta}. \quad (12)$$

Henceforth we identify the phase fields with the volume fractions  $\{\varphi_\alpha\}$ . Once the functions  $\{\mathbf{j}_\alpha\}, \{\tau_\alpha\}$  are specified by constitutive relations, equations (28) may be viewed as a system of first-order differential equations which govern the evolution of  $\{\varphi_\alpha\}$ . This is the main advantage of the present approach in that the evolution equations are provided directly by the continuity equations of the phases. Moreover, the phase fields have a direct physical meaning and determine directly the corresponding mass densities. This scheme, however, is crucially related to the assumption that the phases are incompressible.

If the phases are compressible then the concentrations  $\{c_\alpha\}$  look more convenient (see Morro [11]). In such a case the evolution equations are given by the system (5).

### 3. Binary Mixture

For the sake of formal simplicity, henceforth we restrict attention to binary mixtures,  $n = 2$ . Such is the case for solid-liquid and liquid-vapour transitions. The incompressibility assumption is particularly realistic for the ice-water transition. By (2), (7) and (10) the values of  $\tau_2, \mathbf{j}_2, \varphi_2$  are determined by  $\tau_1, \mathbf{j}_1, \varphi_1$ . To simplify the notation let  $\tau, \mathbf{j}, \varphi$  stand for  $\tau_1, \mathbf{j}_1, \varphi_1$ . Moreover, let  $\rho_i$  stand for  $\bar{\rho}_1$  and  $\rho_w$  for  $\bar{\rho}_2$ . Hence we have

$$\rho_1 = \varphi\rho_i, \quad \rho_2 = (1 - \varphi)\rho_w, \quad c_1 = \frac{\rho_i\varphi}{\rho(\varphi)},$$

where  $\rho(\varphi)$  is the mass density of the mixture and is given by

$$\rho(\varphi) = \varphi\rho_i + (1 - \varphi)\rho_w. \tag{13}$$

Upon substitution we find that the system of equations (28) reduces to

$$\frac{\rho_w\rho_i}{\rho(\varphi)}\dot{\varphi} = -\nabla \cdot \mathbf{j} + \tau. \tag{14}$$

Irrespective of the value of  $\rho_i$  and  $\rho_w$ , the coefficient of  $\dot{\varphi}$  is then a positive-valued function of  $\varphi$ . Moreover, by (13) we find that

$$\dot{\rho} = (\rho_i - \rho_w)\dot{\varphi}. \tag{15}$$

Hence (8) implies that

$$\nabla \cdot \mathbf{v} = \frac{\rho_w - \rho_i}{\rho}\dot{\varphi}. \tag{16}$$

For the ice-water transformation,  $\varphi$  is the ice volume fraction and  $\rho_i < \rho_w$ . As the ice fraction increases,  $\dot{\varphi} > 0$  and, by (15),  $\dot{\rho} < 0$ .

### 3.1. Balance Equations

Following the theory of mixtures, the balance equations for the single phases can be written, as is performed e.g. by Müller [12]. To obtain a simpler model, we are content with the balance of linear momentum and energy for the mixture as a single body. The balance equations are then written as

$$\rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{T} + \rho \mathbf{b}, \quad (17)$$

$$\rho \dot{e} = \mathbf{T} \cdot \mathbf{L} - \nabla \cdot \mathbf{q} + \rho r, \quad (18)$$

where  $\mathbf{T}$  is the Cauchy stress tensor,  $\mathbf{b}$  the body force,  $e$  the internal energy density,  $\mathbf{L}$  the velocity gradient,  $\mathbf{q}$  the heat flux,  $r$  the heat supply. The balance of angular momentum results in the symmetry of  $\mathbf{T}$ .

The second law, or balance of entropy, is taken in a general form which does not force the entropy flux to be equal to the heat flux over the absolute temperature  $\theta$ . Hence we write the second-law inequality as

$$\rho \dot{\eta} \geq -\nabla \cdot \left( \frac{\mathbf{q}}{\theta} + \mathbf{k} \right) + \frac{\rho r}{\theta}, \quad (19)$$

where  $\eta$  is the entropy density and  $\mathbf{k}$  is the extra entropy flux. As the statement of the second law, we assume that the inequality (19) hold for every set of functions on  $\Omega \times \mathbb{R}$  compatible with the balance equations. This means that (17) and (18), as well as (14) and (16) are constraints on  $\mathbf{v}, e, \rho, \varphi$ .

Substitution for  $\rho r - \nabla \cdot \mathbf{q}$  from (18) and use of the free energy density

$$\psi = e - \theta \eta$$

give

$$\rho(\dot{\psi} + \eta\dot{\theta}) - \mathbf{T} \cdot \mathbf{L} - \theta \nabla \cdot \mathbf{k} + \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \leq 0. \quad (20)$$

The extra entropy flux  $\mathbf{k}$  has to be determined so that the inequality (20) holds.

### 3.2. Constitutive Equations

Denote by  $\mathbf{s}$  the displacement field and let  $\mathbf{H} = \nabla \mathbf{s}$ . The dependence on the motion is described by the infinitesimal strain tensor,  $\mathbf{E} = \text{sym} \mathbf{H}$ , and the velocity gradient  $\mathbf{L}$ . Since  $\rho$  is a function of  $\varphi$ , there is no loss in generality in embodying the dependence on  $\rho$  and  $\nabla \rho$  within the dependence on  $\varphi$  and  $\nabla \varphi$ . The effects of the temperature are described by a dependence on  $\theta$  and

$\nabla\theta$ . Higher-order gradients are allowed to occur and hence the dependence on  $\nabla\nabla\theta, \dots, \nabla\mathbf{L}, \nabla\nabla\nabla\theta, \dots, \nabla\nabla\mathbf{L}$ . Accordingly we let

$$\Gamma = (\theta, \varphi, \nabla\theta, \nabla\varphi, \mathbf{E}, \mathbf{L}, \nabla\nabla\theta, \dots, \nabla\nabla\mathbf{L})$$

be the set of independent variables. We express the constitutive equations by saying that  $\psi, \eta, \mathbf{T}, \mathbf{k}, \mathbf{q}, \mathbf{j}, \tau$  are functions of  $\Gamma$ . Moreover,  $\psi, \mathbf{k}, \mathbf{j}$  are continuously differentiable whereas the remaining functions are continuous. To avoid inessential formal difficulties we assume that  $\psi$  be independent of the higher-order gradients and hence let

$$\psi = \psi(\theta, \varphi, \nabla\theta, \nabla\varphi, \mathbf{E}, \mathbf{L}).$$

#### 4. Restrictions on the Constitutive Equations

The analysis of (20) is now performed by accounting for the constraints on the functions  $\mathbf{v}, e, \rho, \varphi$ . In this regard it is convenient to observe that any second-order tensor  $\mathbf{A}$  can be split into the trace,  $\text{tr } \mathbf{A}$ , and the traceless part,  $\overset{\circ}{\mathbf{A}}$ , in the form

$$\mathbf{A} = \frac{1}{3}(\text{tr } \mathbf{A})\mathbf{1} + \overset{\circ}{\mathbf{A}}, \quad \text{tr } \overset{\circ}{\mathbf{A}} = 0.$$

Moreover, for any pair of tensors  $\mathbf{A}, \mathbf{B}$  we have

$$\overset{\circ}{\mathbf{A}} \cdot \mathbf{B} = \overset{\circ}{\mathbf{A}} \cdot \overset{\circ}{\mathbf{B}}.$$

This allows us to write  $\mathbf{L}$  and  $\mathbf{D} = \text{sym}\mathbf{L}$  as

$$\mathbf{L} = \frac{1}{3}(\nabla \cdot \mathbf{v})\mathbf{1} + \overset{\circ}{\mathbf{L}}, \quad \mathbf{D} = \frac{1}{3}(\nabla \cdot \mathbf{v})\mathbf{1} + \overset{\circ}{\mathbf{D}}.$$

Likewise, we write the stress tensor  $\mathbf{T}$  as

$$\mathbf{T} = -p\mathbf{1} + \overset{\circ}{\mathbf{T}},$$

where  $p = -\text{tr } \mathbf{T}/3$ . In inviscid fluids  $p$  coincides with the pressure.

#### 4.1. Identities

Three identities are derived.

For any  $C^2$  function  $\phi$  on  $\Omega \times \mathbb{R}$ , the derivative  $\overline{\nabla \dot{\phi}}$ , of  $\nabla \phi$ , and the gradient  $\nabla \dot{\phi}$  are related by

$$\overline{\nabla \dot{\phi}} = \nabla \dot{\phi} - \mathbf{L}^T \nabla \phi. \quad (21)$$

The result follows by applying the total time derivative and rearranging the terms so that

$$\overline{\nabla \dot{\phi}} = (\partial_t + \mathbf{v} \cdot \nabla) \nabla \phi = \nabla \partial_t \phi + \nabla(\mathbf{v} \cdot \nabla \phi) - (\nabla \mathbf{v}) \nabla \phi = \nabla \dot{\phi} - \mathbf{L}^T \nabla \phi.$$

The derivative  $\dot{\mathbf{E}}$  of the strain and the velocity gradient  $\mathbf{L}$  are related by

$$\dot{\mathbf{E}} = \mathbf{D} - \text{sym}(\mathbf{L}^T \nabla \mathbf{s}). \quad (22)$$

In components, application of the total time derivative and exchange of the order of differentiation yield

$$\begin{aligned} 2\dot{E}_{hk} &= (\partial_t + \mathbf{v} \cdot \nabla)(\partial_k s_h + \partial_h s_k) \\ &= \partial_k \partial_t s_h + \partial_h \partial_t s_k + v_j (\partial_k \partial_j s_h + \partial_h \partial_j s_k) \\ &= \partial_k \partial_t s_h + \partial_h \partial_t s_k + \partial_k v_j \partial_j s_h + \partial_h v_j \partial_j s_k - (\partial_j s_h) \partial_k v_j + (\partial_j s_k) \partial_h v_j \\ &= \partial_k \dot{s}_h + \partial_h \dot{s}_k - (L_{jk} \partial_j s_h + L_{jh} \partial_j s_k). \end{aligned}$$

Since  $\dot{\mathbf{s}} = \mathbf{v}$ , the identity (22) follows.

For any tensor  $\mathbf{A}$ ,

$$\mathbf{A} \cdot \text{sym}(\mathbf{L}^T \nabla \mathbf{s}) = (\nabla \mathbf{s} \mathbf{A}) \cdot \mathbf{L}. \quad (23)$$

Without any loss of generality we let  $\mathbf{A}$  be symmetric. Hence

$$\mathbf{A} \cdot \text{sym}(\mathbf{L}^T \nabla \mathbf{s}) = A_{kh} \frac{1}{2} (L_{jk} \partial_j s_h + L_{jh} \partial_j s_k) = L_{jk} (\partial_j s_h) A_{hk} = \mathbf{L} \cdot (\nabla \mathbf{s} \mathbf{A}).$$

#### 4.2. Thermodynamic Restrictions

Upon substitution in (20), since  $\overset{\circ}{\mathbf{T}} \cdot \mathbf{L} = \overset{\circ}{\mathbf{T}} \cdot \overset{\circ}{\mathbf{L}}$  we have

$$\rho(\dot{\psi} + \eta \dot{\theta}) + p \nabla \cdot \mathbf{v} - \overset{\circ}{\mathbf{T}} \cdot \overset{\circ}{\mathbf{L}} - \theta \nabla \cdot \mathbf{k} + \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \leq 0. \quad (24)$$

Evaluation of  $\dot{\psi}$  and use of the identities (21), (22) yield

$$\rho(\psi_\theta + \eta) \dot{\theta} + \rho \psi_\varphi \dot{\varphi} + \rho \psi_{\nabla \theta} \cdot \overline{\nabla \dot{\theta}} + \rho \psi_{\nabla \varphi} \cdot (\nabla \dot{\varphi} - \mathbf{L}^T \nabla \varphi)$$



$$\begin{aligned}
 & +\rho\psi_{\mathbf{E}} \cdot [\mathbf{D} - \text{sym}(\mathbf{L}^T \nabla \mathbf{s})] + \rho\psi_{\mathbf{L}} \cdot \dot{\mathbf{L}} + p\nabla \cdot \mathbf{v} - \overset{\circ}{\mathbf{T}} \cdot \overset{\circ}{\mathbf{D}} \\
 & -\nabla \cdot (\theta \mathbf{k}) + \mathbf{k} \cdot \nabla \theta + \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \leq 0. \tag{25}
 \end{aligned}$$

The values of  $\dot{\theta}$ ,  $\overset{\circ}{\nabla \theta}$ ,  $\dot{\mathbf{L}}$  occur linearly and can be taken arbitrarily. This implies that (25) holds only if

$$\eta = -\psi_{\theta}, \quad \psi_{\nabla \theta} = 0, \quad \psi_{\mathbf{L}} = 0. \tag{26}$$

The skew part of  $\mathbf{L}$  can be chosen arbitrarily and independently of  $\mathbf{D}$ . Hence by (23), (25) implies that

$$\nabla \varphi \otimes \psi_{\nabla \varphi} + \nabla \mathbf{s} \psi_{\mathbf{E}} \in \text{Sym}.$$

Let

$$\delta_{\mathbf{E}} := \psi_{\mathbf{E}} - \nabla \mathbf{s} \psi_{\mathbf{E}}.$$

The remaining inequality can be written in the form

$$\nabla \cdot (\rho\psi_{\nabla \varphi} \dot{\varphi} - \theta \mathbf{k}) + \mathbf{k} \cdot \nabla \theta + \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta + \Phi \dot{\varphi} - \overset{\circ}{\mathcal{T}} \cdot \overset{\circ}{\mathbf{D}} \leq 0, \tag{27}$$

where

$$\begin{aligned}
 \Phi &= \rho\psi_{\varphi} - \nabla \cdot (\rho\psi_{\nabla \varphi}) + (\rho_w - \rho_i) \left[ \frac{1}{3} \nabla \varphi \cdot \psi_{\nabla \varphi} + \frac{1}{3} \text{tr} \delta_{\mathbf{E}} \psi + \frac{p}{\rho} \right], \\
 \overset{\circ}{\mathcal{T}} &= \overline{\overset{\circ}{\mathbf{T}} + \rho(\nabla \varphi \otimes \psi_{\nabla \varphi} - \delta_{\mathbf{E}} \psi)}.
 \end{aligned}$$

Of course,  $\overset{\circ}{\mathcal{T}} = \overset{\circ}{\mathcal{T}}$ .

The inequality (27) involves  $\dot{\varphi}$  which, by (14) is related to  $\tau$  and  $\mathbf{j}$  by

$$\dot{\varphi} = \alpha(\varphi)(\tau - \nabla \cdot \mathbf{j}), \tag{28}$$

where

$$\alpha(\varphi) = \frac{\rho(\varphi)}{\rho_w \rho_i}.$$

We might replace  $\dot{\varphi}$  in (27) and proceed accordingly but the evaluation of  $\nabla \cdot \mathbf{j}$ ,  $\nabla(\nabla \cdot \mathbf{j})$  and  $\nabla \cdot \mathbf{k}$  leads to a cumbersome relation. It is more convenient to account for the constraint (28) as follows.

Let  $\lambda$  be any function of  $\Gamma$  and insert the zero quantity

$$-\nabla \cdot (\lambda \theta \mathbf{j}) + \theta \mathbf{j} \cdot \nabla \lambda + \theta \lambda \nabla \cdot \mathbf{j} + \lambda \mathbf{j} \cdot \nabla \theta$$

in the left-hand side of (27) to obtain

$$\begin{aligned} \nabla \cdot [\rho\psi_{\nabla\varphi}\dot{\varphi} - \theta(\mathbf{k} + \lambda\mathbf{j})] + (\mathbf{k} + \lambda\mathbf{j}) \cdot \nabla\theta + \theta\mathbf{j} \cdot \nabla\lambda + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta \\ + \Phi\dot{\varphi} + \theta\lambda\nabla \cdot \mathbf{j} - \mathcal{T} \cdot \mathring{\mathbf{D}} \leq 0. \end{aligned} \quad (29)$$

Let

$$\mathbf{w} = \rho\psi_{\nabla\varphi}\dot{\varphi} - \theta(\mathbf{k} + \lambda\mathbf{j})$$

and

$$\tilde{\Phi} = \theta\left[\frac{\rho}{\theta}\psi_{\varphi} - \nabla \cdot \left(\frac{\rho}{\theta}\psi_{\nabla\varphi}\right)\right] + (\rho_w - \rho_i)\left[\frac{1}{3}\nabla\varphi \cdot \psi_{\nabla\varphi} + \frac{1}{3}\text{tr} \delta_{\mathbf{E}}\psi + \frac{p}{\rho}\right].$$

Sufficient conditions for the validity of (29) are given as follows.

**Proposition.** *The inequality (29) holds if*

$$\mathbf{k} = \frac{\rho}{\theta}\psi_{\nabla\varphi}\dot{\varphi} - \frac{\alpha}{\theta}\tilde{\Phi}\mathbf{j}, \quad (30)$$

$$\alpha\tilde{\Phi}\tau + \theta\mathbf{j} \cdot \nabla\left(\frac{\alpha}{\theta}\tilde{\Phi}\right) + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \mathcal{T} \cdot \mathring{\mathbf{D}} \leq 0. \quad (31)$$

*Proof.* Let  $\mathbf{w} = 0$  whence

$$\mathbf{k} = \frac{\rho}{\theta}\psi_{\nabla\varphi}\dot{\varphi} - \lambda\mathbf{j}.$$

Since

$$\mathbf{k} + \lambda\mathbf{j} = \frac{\rho}{\theta}\psi_{\nabla\varphi}\dot{\varphi}$$

then (29) becomes

$$\frac{\rho}{\theta}\psi_{\nabla\varphi}\dot{\varphi} \cdot \nabla\theta + \Phi\dot{\varphi} + \theta\lambda\nabla \cdot \mathbf{j} + \theta\mathbf{j} \cdot \nabla\lambda + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \mathcal{T} \cdot \mathring{\mathbf{D}} \leq 0.$$

Hence, by means of the identity

$$\frac{\rho}{\theta}\psi_{\nabla\varphi} \cdot \nabla\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}) = -\theta\nabla \cdot \left(\frac{\rho}{\theta}\psi_{\nabla\varphi}\right),$$

we can write

$$\tilde{\Phi}\dot{\varphi} + \theta\lambda\nabla \cdot \mathbf{j} + \theta\mathbf{j} \cdot \nabla\lambda + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \mathcal{T} \cdot \mathring{\mathbf{D}} \leq 0.$$

We now make use of (28) to replace  $\dot{\varphi}$  so that

$$(-\tilde{\Phi}\alpha + \theta\lambda)\nabla \cdot \mathbf{j} + \tilde{\Phi}\alpha\tau + \theta\mathbf{j} \cdot \nabla\lambda + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \mathcal{T} \cdot \mathring{\mathbf{D}} \leq 0.$$

Taking advantage of the freedom for  $\lambda$  we let the coefficient of  $\nabla \cdot \mathbf{j}$  be zero by choosing

$$\lambda = \frac{\alpha}{\theta} \tilde{\Phi}.$$

Upon substitution of  $\lambda$ , the remaining inequality takes the form (31).  $\square$

In addition to the classical term  $\mathbf{q} \cdot \nabla \theta / \theta$ , the inequality (31) shows two effects of the incompressibility of the phases. First, the dissipative power of the stress is given by  $\mathcal{T} \cdot \overset{\circ}{\mathbf{D}}$ . The tensor  $\mathcal{T}$  equals the (deviatoric part of the) stress  $\mathbf{T}$  deprived of the elastic stress  $\rho \delta_{\mathbf{E}} \psi$  and the stress  $\rho(\nabla \varphi \otimes \psi_{\nabla \varphi})$ . The term  $\nabla_{\mathbf{s}} \psi_{\mathbf{E}}$  disappears in linear theories whereas  $\nabla \varphi \otimes \psi_{\nabla \varphi}$  accounts for the inhomogeneity of the order parameter (see Gurtin et al [9], Morro [10]). Secondly, the scalar-valued function  $\tilde{\Phi}$ , which enters both the dissipation inequality (31) and the extra entropy flux (30) consists of two parts. One of them,

$$(\rho_w - \rho_i) \left[ \frac{1}{3} \nabla \varphi \cdot \psi_{\nabla \varphi} + \frac{1}{3} \text{tr} \delta_{\mathbf{E}} \psi + \frac{p}{\rho} \right],$$

arises because of the incompressibility. The other,

$$\theta \left[ \frac{\rho}{\theta} \psi_{\varphi} - \nabla \cdot \left( \frac{\rho}{\theta} \psi_{\nabla \varphi} \right) \right],$$

can be viewed as the integrand of the variational derivative, with respect to  $\varphi$ , of the rescaled free energy

$$\tilde{\Psi} = \int_{\Omega} \frac{\rho}{\theta} \psi(\theta, \varphi, \mathbf{E}, \nabla \varphi) dv.$$

The rescaling through the factor  $1/\theta$  occurs also in other models (see Alt et al [1]) and is introduced by Brokate et al [4].

### 5. Evolution Equation

The validity of (26), (30) and (31) is sufficient for the compatibility of the functions  $\psi, \eta, \mathbf{k}, \mathbf{q}, \mathbf{T}, \mathbf{j}, \tau$  with the second law of thermodynamics. For definiteness we now look at a simple case which is sufficient for the validity of (31). Let each term in (31) satisfy, per se, the inequality namely

$$\tilde{\Phi} \tau \leq 0, \quad \mathbf{j} \cdot \left( \frac{\alpha}{\theta} \tilde{\Phi} \right) \leq 0, \tag{32}$$

$$\mathbf{q} \cdot \nabla \theta \leq 0, \quad \mathcal{T} \cdot \overset{\circ}{\mathbf{D}} \geq 0. \tag{33}$$

The inequalities (33) are the classical ones for heat conduction and mechanical dissipation, though for the trace-free stress  $\mathcal{T}$  only. The Fourier-type law  $\mathbf{q} = -k\nabla\theta$  satisfies the heat conduction inequality provided  $k$  is any positive-valued function of  $\Gamma$ . The dependence of  $\mathcal{T}$  on  $\overset{\circ}{\mathbf{D}}$ , satisfying (33) is

$$\overset{\circ}{\mathcal{T}} = \mu \overset{\circ}{\mathbf{D}}, \quad \mu > 0,$$

$\mu$  being any positive-valued function of  $\Gamma$ . Hence

$$\overset{\circ}{\mathbf{T}} = \rho \overline{(\delta_{\mathbf{E}}\psi - \nabla\varphi \otimes \psi_{\nabla\varphi})} + \mu \overset{\circ}{\mathbf{D}}.$$

The traceless stress  $\overset{\circ}{\mathbf{T}}$  consists of three terms: (the traceless part of) the elastic part  $\rho\delta_{\mathbf{E}}\psi$ , the viscous part  $\mu\mathbf{D}$ , and  $-\rho(\nabla\varphi \otimes \psi_{\nabla\varphi})$ , due to the inhomogeneity of the phase field in a deformable body (see Gurtin et al [9], Morro [4]).

The inequalities (32) are satisfied by

$$\tau = -\beta\tilde{\Phi}, \quad \mathbf{j} = -\gamma\nabla\left(\frac{\alpha}{\theta}\tilde{\Phi}\right),$$

$\beta, \gamma$  being positive-valued functions of  $\Gamma$ . This means that the growth  $\tau$  is governed by  $\tilde{\Phi}$  whereas  $\alpha\tilde{\Phi}/\theta$  governs the diffusion flux  $\mathbf{j}$ .

By (28), the evolution of the order parameter  $\varphi$  is given by

$$\dot{\varphi} = -\alpha[\beta\tilde{\Phi} - \nabla \cdot \left(\frac{\gamma\alpha}{\theta}\tilde{\Phi}\right)].$$

The evolution is then characterized by the two functions  $\beta, \gamma$  which, in the simplest model, are regarded as constants.

## 6. Free Energy and Clapeyron's Equation

The solid and liquid phases are taken to be described by the free energy densities  $\psi^s(\theta, \mathbf{E})$  and  $\psi^l(\theta)$ . By analogy, e.g., with Wang et al [13], we take  $\psi$  in the form

$$\psi(\theta, \varphi, \nabla\varphi, \mathbf{E}) = \psi^l(\theta) + h(\varphi)[\psi^s(\theta, \mathbf{E}) - \psi^l(\theta)] + G(\varphi) + \alpha|\nabla\varphi|^2, \quad (34)$$

where  $\alpha > 0$  and  $h$  is a monotone-increasing, differentiable function such that

$$h(0) = 0, \quad h(1) = 1.$$

For definiteness and simplicity we let  $h(\varphi) = \varphi$ . The function  $G$  is a double-well potential with two equal minima at  $\varphi = 0, 1$ ; to fix ideas, let

$$G(0) = G(1) = 0.$$

We have

$$\psi(\theta, 0, \mathbf{E}) = \psi_l(\theta), \quad \psi(\theta, 1, \mathbf{E}) = \psi_s(\theta, \mathbf{E}).$$

The entropy density is given by

$$\eta = -\psi_\theta = (\varphi - 1)\eta^l(\theta) - \varphi\eta^s(\theta, \mathbf{E}),$$

where

$$\eta^l(\theta) = -\frac{\partial\psi^l(\theta)}{\partial\theta}, \quad \eta^s(\theta, \mathbf{E}) = -\frac{\partial\psi^s(\theta, \mathbf{E})}{\partial\theta}.$$

The latent heat  $L$  is defined by the entropy  $\eta(\theta, \varphi, \mathbf{E})$  as

$$L = \theta_c[\eta(\theta_c, 0, \mathbf{E}) - \eta(\theta_c, 1, \mathbf{E})],$$

where  $\theta_c$  is the value of  $\theta$  at which the transition occurs. Hence

$$L = \theta_c[\eta^l(\theta_c) - \eta^s(\theta_c, \mathbf{E})]. \tag{35}$$

The different value of the entropy in the two phases provides the non-zero value of the latent heat. Replacing  $G(\varphi) \rightarrow f(\theta)G(\varphi)$ , for any function  $f$ , changes the entropy function but not the latent heat.

### 6.1. Clapeyron's Equation

It is usually derived and applied for the equilibrium between liquid and vapour. By the same token, it is said to characterize the equilibrium between the liquid and solid phases (see Fermi [6], p. 68). Consistent with standard thermodynamic approaches, the deformation of the solid ( $\mathbf{E}$ ) is disregarded.

Equilibrium between the two phases is characterized by requiring that  $\varphi$  be constant and hence that the mass growth  $\tau$  be zero. This amounts to

$$\rho\psi_\varphi + (\rho^l - \rho^s)\frac{p}{\rho} = 0, \tag{36}$$

where  $\rho = \rho(\varphi)$  and  $p = p(\theta, \varphi)$ . By (34) we have

$$\psi_\varphi(\theta, \varphi) = \psi^s(\theta, \varphi) - \psi^l(\theta, \varphi) + G'(\varphi)$$

and hence (36) becomes

$$\rho^2(\varphi)[\psi^s(\theta, \varphi) - \psi^l(\theta, \varphi) + G'(\varphi)] + (\rho^l - \rho^s)p(\theta, \varphi) = 0.$$

Along any phase equilibrium line  $\varphi$  is constant. The point (or state) on the equilibrium line varies by changing the temperature  $\theta$  and then the pressure  $p$  accordingly. Differentiation with respect to  $\theta$  (at constant  $\varphi$ ) gives

$$\frac{\partial p}{\partial \theta} = \frac{\rho^2}{\rho^s - \rho^l} \frac{\partial}{\partial \theta} [\psi^s(\theta) - \psi^l(\theta)],$$

the dependence on  $\varphi$  being understood. By (35) we can write

$$\frac{\partial p}{\partial \theta} = \frac{\rho^2}{\rho^s - \rho^l} \frac{L}{\theta}.$$

Now,

$$\frac{\rho^2}{\rho^s - \rho^l} = \frac{\rho^s \rho^l}{\rho^s - \rho^l} \frac{\rho^2}{\rho^s \rho^l} = \frac{1}{1/\rho^l - 1/\rho^s} [\varphi + (1 - \varphi) \frac{\rho^l}{\rho^s}] [\varphi \frac{\rho^s}{\rho^l} + 1 - \varphi].$$

This shows that  $dp/d\theta$  changes as the fraction  $\varphi$  varies namely in passing from the solid to the liquid phase.

If  $\rho^l/\rho^s \simeq 1$  then

$$[\varphi + (1 - \varphi) \frac{\rho^l}{\rho^s}] [\varphi \frac{\rho^s}{\rho^l} + 1 - \varphi] \simeq 1.$$

With such an approximation we have

$$\frac{\partial p}{\partial \theta} = \frac{L}{\theta(1/\rho^l - 1/\rho^s)}. \quad (37)$$

Equation (37) is the standard form of Clapeyron's equation. For the ice-water transition we have  $\rho^l > \rho^s$  and hence we obtain the well-known condition

$$\frac{\partial p}{\partial \theta} < 0$$

for the ice-water equilibrium.

Incidentally, letting  $G(\varphi) \rightarrow f(\theta)G(\varphi)$  in (34) would provide the change  $L \rightarrow L + \theta f'(\theta)G'(\varphi)$  in (37), which does not seem to be motivated on a physical ground.

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