



THE CLAUSIUS–CLAPEYRON EQUATIONS FOR PHASE TRANSITIONS OF THE FIRST KIND IN A THERMOELASTIC MATERIAL†

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A model of the quasi-stationary isothermal phase transitions of thermoelastic solids is considered. Some problems connected with the specification of the kinematic characteristic of the phase transition are discussed. Relations on the surface of a strong discontinuity separating the phases of the material are formulated. Unlike the classical case of the equilibrium of liquid (gas) phases, the proposed relations take into account the irreversible nature of the transition in solids, the tensor character of the chemical potential and the important dependence on the type of anisotropy of the material of the phases. The Clausius–Clapeyron equations are formulated for a thermoelastic medium with arbitrary symmetry; these determine expressions for the derivatives of the phase-transition temperature with respect to the initial strain and orientation of the surface. These equations enable the investigation of the neighbourhood of the jump in the space of initial parameters to be investigated. For the case of an initially isotropic material it is shown that the normal to the interface, which coincides with one of the principal axes of the tensor of finite deformation of the initial phase, yields an extremum of the phase transition temperature for a fixed strain of the initial phase. The phase transition of the first kind in a linear initially isotropic thermoelastic material is investigated in detail. It is shown that the smallness of the deformations of each of the phases implies smallness of the jump, which experiences rotation of the material particle on the phase boundary. A class of materials for which, when there is a change in the deformation of the initial phase, the type of the phase transition inevitably changes, i.e. a transition occurs from a normal phase transition to an anomalous transition, is discussed. © 2004 Elsevier Ltd. All rights reserved.

Experiment shows that practically all materials experience phase transitions when subjected to intense thermal and mechanical loads. From the point of view of continuum mechanics, these transitions can be treated as a manifestation of the non-uniqueness of the response functions (functionals) of the material and can be modelled as a transition from one branch of the reaction to another. In this case one can use the constitutive equations of the “normal” material of each of the phases, in particular, convex thermodynamic potentials. An alternative approach to investigating phase transitions is based on the assumption that a single equation of state exists, which does not possess the properties of convexity in a certain range of the parameters of state. A classical example is the van-der-Waals equation [1]. Starting from [2], a non-convex equation of state is also widely used in models of phase transitions of solids. The main drawback of these equations is that it is impossible to obtain practical information on the behaviour of the material at points at which the Hadamard condition [3], which is necessary for the boundary-value problems to the well posed, breaks down.

A phase transition can occur when the nucleus of a new phase is formed. If, for reasons of an energy nature, the growth of the nucleus of a new phase is limited to mesodimensions that are small compared with the dimensions of the body, a mixture of two phases is formed with a compositional structure of the material, consisting of a “matrix” of the initial phase, “reinforced” by inclusions of the new phase scattered throughout the volume of the solid. In addition to the problem of the effective properties of such a medium, traditional for the mechanics of composite materials, there is a problem of a phenomenological description of the actual concentration and spatial distribution of the inclusions depending on the prehistory of the stresses and the thermal state [4].

When there is an unlimited increase in the nuclei, macroscopic regions are formed each of which occupies one of the phases. The interface is the surface of discontinuity of certain thermodynamic potentials of the medium and their first derivatives. Following the generally accepted terminology, we will call this case a phase transition of the first kind and we will consider this case only. The main problems when investigating such transitions are to establish relations for the jumps in the quantities at the interface and to analyse the stability of the interface.

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These discontinuities have been investigated in detail for the case of thermal and mechanical equilibrium of the phases of an ideal liquid (gas) [2, 5]. The difficulties in modelling phase transitions of solids is due to the fact that the state and response of such materials comprise a more complex set of variables, including strain and stress tensors. Moreover, the phases of a solid, in general, have a different type of anisotropy, which requires different undistorted configurations in order to formulate the constitutive equations of the phases. An important difference is also related to the nature of the dissipative processes in solids. For liquids in zones of high gradients, the main dissipative mechanisms are viscosity and heat conduction, which lead to Navier–Stokes type equations with an infinitesimal memory of the medium concerning past states. For solids, the main dissipative mechanisms in zones of high gradient are related to the effects of plasticity, which is characterized by a long or even non-fading memory of the material. This difference leads to the fact that, on the slowly moving surfaces which separate the phases of a liquid, the entropy production is small, while for solids the contribution of singular sources of entropy, concentrated at the interface, may be considerable. The phenomenon of hysteresis of phase transitions in solids [6], in particular, indicates this.

During the last ten years, a number of problems have been solved in the phenomenological theory of phase transitions in solids, close to a state of thermal and mechanical equilibrium. These include, in the first place, the rejection of attempts to determine the scalar chemical potential for a solid and a transition to chemical potential tensors [7–14]. For certain boundary conditions, the stability of the motion of the discontinuities considered has been investigated [8, 14]. As in the theory of shock waves [15], the kinetics of the phase transition play an important role [16–18]. These determine, in particular, the structure and stability of a strong discontinuity. Consideration of the kinetics enables the phase transition of solids to be considered from the position of more general rheological relations, for which there is a continuous thermomechanical history of the element of the material, undergoing a transition, rather than a sudden one.

Research shows that the tensor nature of the chemical potential and the irreversible nature of the phase transition in a thermoelastic body, which are not entirely taken into account in [19], have a considerable influence on the dependence of the phase-transition temperature on the deformation of the initial phase and orientation of the interface.

1. THE KINEMATICS OF BODIES WITH PHASE TRANSITIONS

We will consider the kinematics of a thermoelastic solid, the finite deformations and arbitrary heating of which are accompanied by phase transitions. The phases are assumed, in general, to be anisotropic solid materials with different types of anisotropy. We will use three configurations of the body: $\kappa_0^{(n)}$ ($n = 1, 2$) are undistorted reference configurations of the body in the n -th phase state, $\chi(t)$ is the actual configuration, which is either completely occupied by one of the phase, or two phases can coexist in it, separated by an interface. To fix our ideas, suppose the configurations $\kappa_0^{(n)}$ are natural (unstressed) at the same temperature $\theta_0 = \text{const}$. In the n -th phase state the material possesses group symmetry $g_{\kappa_0^{(n)}} \in o$, where o is the natural orthogonal group [3]. In other words, the constitutive equations of the material of the n -th phase, written using deformations, measured from the initial configuration $\kappa_0^{(n)}$, will be invariant under orthogonal transformations, which occur in the group $g_{\kappa_0^{(n)}}$.

We will put $\rho_{\kappa}^{(n)}(\theta_0) = \text{const}$ – the density of the material in the configuration $\kappa_0^{(n)}$, where, in general, $\rho_{\kappa}^{(1)} \neq \rho_{\kappa}^{(2)}$. Suppose $d\mathbf{x}$, $d\mathbf{X}^{(n)}$ are radius vectors connecting two infinitesimally close particles in the configurations $\chi(t)$ and $\kappa_0^{(n)}$, respectively, and connected by the non-degenerate transformations

$$\begin{aligned} d\mathbf{x} &= \mathbf{F}^{(1)} \cdot d\mathbf{X}^{(1)} = \mathbf{F}^{(2)} \cdot d\mathbf{X}^{(2)}, \quad \det \mathbf{F}^{(1)} > 0, \quad \det \mathbf{F}^{(2)} > 0 \\ d\mathbf{X}^{(1)} &= \mathbf{F}_0 \cdot d\mathbf{X}^{(2)}, \quad \det \mathbf{F}_0 > 0, \quad \mathbf{F}_0 = \mathbf{R}_0 \cdot \mathbf{U}_0 \end{aligned} \quad (1.1)$$

where $\mathbf{F}^{(n)}$ is the gradient of the mappings $\kappa_0^{(n)} \rightarrow \chi(t)$, and \mathbf{F}_0 is the gradient of the mapping $\kappa_0^{(2)} \rightarrow \kappa_0^{(1)}$, \mathbf{R}_0 is an orthogonal tensor and \mathbf{U}_0 is a symmetrical positive-definite tensor. From relations (1.1) we have

$$\mathbf{F}^{(2)} = \mathbf{F}^{(1)} \cdot \mathbf{F}_0 \quad (1.2)$$

the tensor \mathbf{F}_0 is the kinematic characteristic of the phase transition in the solid [13], which must be specified when constructing a model of the phase transitions. In the classical theory of phase transitions [1, 5], the analogue of \mathbf{F}_0 is the ratio of the densities of the material (the specific volumes) of the phases for a specified pressure and a specified thermal state.

In the configurations $\kappa_0^{(n)}$ the phases of the material differ not only in the mass density and type of anisotropy, but also in the densities of the free energy and entropy. The difference in the free energy and the difference in the entropy of the phases in the configurations $\kappa_0^{(n)}$ are rheological characteristics of a phase transition of the first kind in solids [13]. These characteristics, like the tensor \mathbf{F}_0 , depend on the temperature and stresses in the configurations $\kappa_0^{(n)}$.

The question arises – what a priori limitations are imposed on the non-degenerate tensor \mathbf{F}_0 ? Even in the simplest case, when both phases are initially isotropic materials, the assertion that the configurations $\kappa_0^{(1)}$ and $\kappa_0^{(2)}$ are related by a similitude transformation ($\mathbf{U}_0 = \alpha \mathbf{I}$, $\alpha > 0$) is an assumption which does not follow directly from the property of the initial isotropy of each of the phases of the material. In the case of anisotropy of the material of the phases the situation is even more complicated.

We will start from the hypothesis that the mapping $\kappa_0^{(2)} \rightarrow \kappa_0^{(1)}$ satisfies the condition

$$\det \mathbf{F}_0 = \rho_{\kappa}^{(2)} / \rho_{\kappa}^{(1)} \quad (1.3)$$

and corresponds to a minimum of the free energy density of the second phase $\psi^{(2)}(\mathbf{F}^{(2)}, \theta_0)$ in the configuration $\kappa_0^{(1)}$, i.e. when $\mathbf{F}^{(2)} = \mathbf{F}_0$. The necessary condition for this hypothesis to be satisfied is

$$\left. \frac{\partial}{\partial \mathbf{F}^{(2)}} \left(\psi^{(2)}(\mathbf{F}^{(2)}, \theta_0) - \beta \left(J(\mathbf{F}^{(2)}) - \frac{\rho_{\kappa}^{(2)}}{\rho_{\kappa}^{(1)}} \right) \right) \right|_{\mathbf{F}^{(2)} = \mathbf{F}_0} = 0 \quad (1.4)$$

where β is a Lagrange multiplier, determined from constraints (1.3) on the deformation \mathbf{F}_0 , and $J^{(2)} = \det \mathbf{F}^{(2)}$. Taking into account the formulae (\mathbf{T} is a symmetric Cauchy stress tensor)

$$\rho_{\kappa}^{(2)} = \frac{\partial \psi^{(2)}(\mathbf{F}^{(2)}, \theta)}{\partial \mathbf{F}^{(2)}} = J^{(2)} \mathbf{T}^{(2)} \cdot \mathbf{F}^{(2)-1T}, \quad \frac{\partial J^{(2)}}{\partial \mathbf{F}^{(2)}} = J^{(2)} \mathbf{F}^{(2)-1T}$$

it follows from condition (1.4) that the stress tensor of the second phase in the configuration $\kappa_0^{(1)}$ is spherical

$$\mathbf{T}^{(2)}(\mathbf{F}_0, \theta_0) = \beta \rho_{\kappa}^{(2)} \mathbf{I}$$

Using the representation for the stress tensor of an elastic material with an arbitrary type of anisotropy

$$\mathbf{T}^{(2)}(\mathbf{F}_0, \theta_0) = \mathbf{R}_0 \cdot \mathbf{T}^+(\mathbf{U}_0, \theta_0) \cdot \mathbf{R}_0^T$$

which is necessary for the constitutive equation to be independent of the choice of the frame of reference [3], we obtain

$$\mathbf{T}^+(\mathbf{U}_0, \theta_0) = \beta \rho_{\kappa}^{(2)} \mathbf{I} \quad (1.5)$$

Relation (1.5), together with the condition (1.3), gives a system of equations for determining \mathbf{U}_0 .

The spherical tensor (1.5) is a special case of the stressed states of undistorted configurations, generated by transformations of the natural (unstressed) configuration. Hence, provided that $\mathbf{T}^+(\mathbf{U}_0, \theta_0)$ is a one-to-one function of the tensor \mathbf{U}_0 , the configuration $\kappa_0^{(1)}$ will also be undistorted for the second phase. The symmetry group of the material of the second phase in this configuration

$$\hat{g}_{\kappa_0}^{(2)} = \mathbf{R}_0^T g_{\kappa_0}^{(2)} \mathbf{R}_0$$

is an orthogonally conjugate group $g_{\kappa_0}^{(2)}$, while the tensor \mathbf{U}_0 commutes with any element $\mathbf{G} \in g_{\kappa_0}^{(2)}$ [3]. Examples of such tensors are $\mathbf{U}_0 = a \mathbf{I} + b \mathbf{n} \otimes \mathbf{n}$ for a transversely-isotropic material, and $\mathbf{U}_0 = a \mathbf{k} \otimes \mathbf{k} + b \mathbf{m} \otimes \mathbf{m} + c \mathbf{n} \otimes \mathbf{n}$ for an orthotropic material. Here \mathbf{I} is the unit tensor, \mathbf{k} , \mathbf{m} and \mathbf{n} are mutually orthogonal vectors, defining the direction of the crystallographic axes, and the scalar parameter $a, b, c > 0$.

It should be noted that the natural configuration $\kappa_0^{(2)}$ can be regarded as a configuration which is obtained from the actual configuration $\chi(t)$ by unloading each element of the body on the assumption that all points of the body are in the second phase state and that phase transitions do not occur during unloading. Since the tensor \mathbf{U}_0 defined by Eqs (1.3) and (1.5) is constant, the configuration $\kappa_0^{(2)}$, like

$\kappa_0^{(1)}$, will belong to a three-dimensional Euclidean space. We emphasise that the result obtained holds for a uniform kinematic characteristic of the phase transition. If the kinematic characteristic of U_0 is non-uniform in space, and does not satisfy the compatibility equation [20, 21], $\kappa_0^{(2)}$ will be non-Euclidean.

Hence, the kinematics of the phase transitions of solids possesses a certain similarity with the kinematics of plastic flow. The kinematics of a material element, subjected to finite plastic deformation, is a representation which connects the reference, actual and unloaded configurations with one another. The gradient of the mapping of the reference configuration into the actual configuration can be represented in the form of a composition of gradients of the "elastic" and "plastic" representations [21–23]. For non-uniform plastic deformation the unloaded configuration, in general, is non-Euclidean.

The main difference between the kinematics of phase transitions and the kinematics of plastic flow is the fact that plastic deformation depends on the applied loads and varies with time, whereas the kinematic characteristic of the phase transition is constant. In this plan, the kinematics of phase transitions is simpler compared with the kinematics of plastic deformations.

This analogy becomes closer when the kinetics of the phase transitions of solids is taken into account, when the degree of transition is variable in space and time, while the kinematic characteristic is related to the limiting position of an intermediate configuration, corresponding to complete transition of an element into the second phase state.

2. RELATIONS AT THE INTERFACE

On the assumption that the process is close to equilibrium, we will formulate relations on the surface of the strong discontinuity which separates the phases of the material. Two relations are obvious: continuity of the temperature

$$[\theta] = 0 \quad (2.1)$$

and continuity of the radius vector \mathbf{x} , defining the position of a material particle in the actual configuration $\chi(t)$ of the body at the instant of time t

$$[\mathbf{x}] = 0 \quad (2.2)$$

Condition (2.2) is sometimes considered as the definition of coherent phase transitions [8, 9]. Examples of such transitions are twinning processes [24, 25] and some transitions in quartz [26, 27]. Sometimes models of non-coherent phase transitions are considered [8], for which continuity is assumed only for the normal component of the jump in the vector \mathbf{x} . If we consider not only equilibrium, stationary phase boundaries but also those that move with respect to the particles, then, within the framework of the systematic quasi-static model these transitions cannot be realized since the jump in the tangential component of the velocity in such transitions will be large and, as a consequence, the inertial forces will be substantial.

To derive the remaining relations on a strong discontinuity we can use the integral relation [10, 13], written in material variables $\mathbf{X} \equiv \mathbf{X}^{(1)} \in \kappa_0^{(1)}$

$$\frac{d}{dt} \int_{\kappa} \rho_{\kappa} \varphi_{\kappa} dV_{\kappa} = \int_{\partial \kappa} \mathbf{n}_{\kappa} \cdot \Phi_{\kappa} dS_{\kappa} + \int_{\kappa} \rho_{\kappa} f dV_{\kappa} + \int_{S_0} \rho_{\kappa} c_{\kappa} \zeta dS_0 \quad (2.3)$$

Equation (2.3) includes the equation of equilibrium, the law of conservation of energy, the divergent equation of compatibility of the deformations and velocities [21, 28] and the entropy balance equation. We will take into account the presence in the body of a strong discontinuity surface $S_0(t)$, moving with velocity c_{κ} , on which a certain contribution to the balance relation can occur

$$\varphi_{\kappa} = \begin{Bmatrix} 0 \\ u \\ \mathbf{F}^T \\ \eta \end{Bmatrix}, \quad \Phi_{\kappa} = \begin{Bmatrix} \mathbf{T}_{\kappa}^T \\ \mathbf{T}_{\kappa}^T \cdot \mathbf{v} - \mathbf{q}_{\kappa} \\ \mathbf{I} \otimes \mathbf{v} \\ -\mathbf{q}_{\kappa}/\theta \end{Bmatrix}, \quad f = \begin{Bmatrix} \mathbf{b} \\ \mathbf{b} \cdot \mathbf{v} + r \\ 0 \\ r/\theta \end{Bmatrix}, \quad \zeta = \begin{Bmatrix} 0 \\ 0 \\ 0 \\ \delta_* \end{Bmatrix} \quad (2.4)$$

where \mathbf{F} is the gradient of the mapping $\kappa_0^{(1)} \rightarrow \chi(t)$, $J = \det \mathbf{F} > 0$, $\mathbf{T}_{\kappa} = J \mathbf{T} \cdot \mathbf{F}^{-1T}$ is an asymmetric

Piola–Kirchhoff strain tensor, u and η are the internal energy and entropy densities, $\mathbf{q}_\kappa = J\mathbf{F}^{-1} \cdot \mathbf{q}$ is the Lagrange vector of the heat flux, and ζ is the amplitude of singular sources of the δ -function type with a carrier on $S_0(t)$.

The set of assumptions regarding the amplitudes of these sources for a system of conservation laws is an independent part of any model of a continuous medium, which allow of discontinuous solutions [15]. We will assume that there are no singular sources of mass, momentum and energy on the moving surfaces of strong discontinuities, which separate the two phases of the material, as in the classical theory of shock waves. The absence of sources of incompatibility of deformations follows from relation (2.2). As regards the singular source of entropy δ_* , its absence on the interface in a solid is not obvious. Moreover, the phenomenon of hysteresis of phase transitions in elastic solids [6], which do not manifest considerable plastic (viscous) deformations in the volume of the body, indicates the presence of such sources more quickly. Hence, the case $\delta_* = 0$ will be called a reversible phase transition, for the irreversible phase transition $\delta_* > 0$.

From system (2.3) we obtain relations for the jumps at the interface (c_κ is the velocity of motion and \mathbf{n}_κ is the normal)

$$\rho_\kappa c_\kappa [\Phi_\kappa] + \mathbf{n}_\kappa \cdot [\mathbf{\Phi}_\kappa] + \rho_\kappa c_\kappa \zeta = 0$$

Taking expressions (2.4) into account, we will write these relations in expanded form

$$[\mathbf{T}_\kappa] \cdot \mathbf{n}_\kappa = 0 \quad (2.5)$$

$$\rho_\kappa c_\kappa [u] + [\mathbf{v} \cdot \mathbf{T}_\kappa] \cdot \mathbf{n}_\kappa - [\mathbf{q}_\kappa] \cdot \mathbf{n}_\kappa = 0 \quad (2.6)$$

$$[\mathbf{F}] = \mathbf{h}_\kappa \otimes \mathbf{n}_\kappa, \quad \mathbf{h}_\kappa \equiv -[\mathbf{v}]/c_\kappa \quad (2.7)$$

$$\rho_\kappa c_\kappa [\theta\eta] - [\mathbf{q}_\kappa] \cdot \mathbf{n}_\kappa + \rho_\kappa c_\kappa \delta_* = 0 \quad (2.8)$$

Relation (2.5) is the condition for continuity of the stress vector at the interface. Relation (2.7) is a consequence of the continuity of the vector $\mathbf{x}(\mathbf{X}, t)$ at the interface and, in addition, of the diad structure of the tensor $[\mathbf{F}]$ and indicates that there is no singular source of incompatibility of the deformations and velocities. Taking relation (2.1) into account, it follows from Eqs (2.6) and (2.8) [13] that, for a phase transition of a thermoelastic material, the jump in the free energy is equal to the sum of the dissipation density and the work of the stress vector on the strong discontinuity.

$$[\psi] = \rho_\kappa^{-1} \mathbf{h}_\kappa \cdot \mathbf{T}_\kappa \cdot \mathbf{n}_\kappa + \delta_* \quad (2.9)$$

Relation (2.9) is the analogue of the equation of the chemical potentials in the classical theory [1, 5] of the equilibrium of the phases of an ideal liquid, but differs considerably in the fact that it is the condition of continuity of the normal components of the *Lagrange tensor of the chemical potential* [7–10]

$$\mathbf{n}_\kappa \cdot [\boldsymbol{\chi}_\kappa] \cdot \mathbf{n}_\kappa = 0, \quad \boldsymbol{\chi}_\kappa \equiv \rho_\kappa (\psi - \delta_*) \mathbf{I} - 1/2 (\mathbf{F}^T \cdot \mathbf{T}_\kappa + \mathbf{T}_\kappa^T \cdot \mathbf{F}) \quad (2.10)$$

In Euler variables $\mathbf{x} \in \chi(t)$ the relations for the jumps in the quantities at an interface moving with velocity c with respect to the particles of the medium and possessing a normal \mathbf{n} , have the form

$$[\rho c] = 0 \quad (2.11)$$

$$[\mathbf{T}] \cdot \mathbf{n} = 0 \quad (2.12)$$

$$\rho c [u] + [\mathbf{v} \cdot \mathbf{T} - \mathbf{q}] \cdot \mathbf{n} = 0 \quad (2.13)$$

$$[\mathbf{F}] = \mathbf{h} \otimes J^{-1} \mathbf{F}^T \cdot \mathbf{n}, \quad \mathbf{h} \equiv -\rho_\kappa [\mathbf{v}]/(\rho c) \quad (2.14)$$

$$\rho c [\theta\eta] - [\mathbf{q}] \cdot \mathbf{n} + \rho c \delta_* = 0 \quad (2.15)$$

Relation (2.11) is the condition of continuity of the mass flow. Equation (2.12) is the condition of continuity of the stress vector, written using the Cauchy stress tensor \mathbf{T} . Relation (2.14) is a consequence

of the equation of compatibility of the deformations [21, 28] in Euler variables. It follows from relations (2.13) and (2.15) that

$$[\psi] = \rho_{\kappa}^{-1} \mathbf{h} \cdot \mathbf{T} \cdot \mathbf{n} + \delta_* \quad (2.16)$$

or

$$\mathbf{n} \cdot [\chi] \cdot \mathbf{n} = 0, \quad \chi \equiv (\psi - \delta_*) J^{-2} \mathbf{B} - \frac{1}{2\rho_{\kappa} J} (\mathbf{B} \cdot \mathbf{T} + \mathbf{T} \cdot \mathbf{B}) \quad (2.17)$$

Here χ is the Euler chemical potential tensor, connected with the Lagrange tensor (2.10) by the simple relation $\chi = J^{-2} \mathbf{F} \cdot \chi_{\kappa} \cdot \mathbf{F}^T$

The dissipation δ_* in expressions (2.9), (2.10), (2.16) and (2.17) enables the hysteresis of the phase transitions of elastic solids to be described in a natural way. To illustrate this consider a one-dimensional continuum (a cylindrical rod) in the isothermal approximation. The material of the rod can be in two phase states. The difference in the moduli of elasticity of the material of the phases is assumed to be small compared with the modulus of elasticity of the initial phase. The elastic potentials and the relation between the stresses and strains of the initial and generated phase are given by the expressions

$$\begin{aligned} u_1(e) &= \frac{1}{2} E e^2 = \frac{1}{2} \sigma^2 / E, \quad \sigma = E e \\ u_2(e) &= u_0 + \frac{1}{2} E (e - e_0)^2 = u_0 + \frac{1}{2} \sigma^2 / E, \quad \sigma = E(e - e_0), \quad e \geq e_0 \end{aligned} \quad (2.18)$$

Here σ is the stress, e is the strain, $E > 0$ is Young's modulus, u_0 is the latent energy of the phase transition and e_0 is a kinematic characteristic of the phase transition, equal to the strain, for which the stress in the material of the second phase vanishes.

In the problem considered, condition (2.12) of the continuity of the stresses and the energy condition (2.16) serve as the conditions of equilibrium, which can be written in the form

$$\sigma_1 = \sigma_2, \quad u_2 - u_1 = \sigma_1(e_2 - e_1) - \delta_*$$

Taking formulae (2.18) into account, these relations give a system of two equations in e_1 and e_2

$$e_2 - e_1 = e_0, \quad u_0 + \delta_* = \sigma_0 e_1, \quad \sigma_0 \equiv E e_0$$

Hence it follows that

$$e_1 = (u_0 + \delta_*) / \sigma_0, \quad e_2 = e_1 + e_0, \quad \sigma^{(12)} = (u_0 + \delta_*) / e_0 \quad (2.19)$$

where $\sigma^{(12)}$ is the stress for which a direct phase transition occurs.

For the inverse phase transition, when a phase transition wave propagates in the second phase, we have

$$\sigma_1 = \sigma_2, \quad u_2 - u_1 = \sigma_1(e_2 - e_1) + \delta_*$$

Hence, taking expressions (2.18) into account, we find that the stress $\sigma^{(21)}$, for which an inverse phase transition occurs, is given by the equation

$$\sigma^{(21)} = (u_0 - \delta_*) / e_0 \quad (2.20)$$

We seen from formulae (2.19) and (2.20) that the value of the singular source of dissipation is proportional to the difference in the stresses of the direct and inverse phase transitions

$$\sigma^{(12)} - \sigma^{(21)} = 2\delta_*/e_0 > 0.$$

3. THE CLAUSIUS-CLAPEYRON EQUATIONS

Consider the system of equations consisting of the condition of continuity (2.5) of the stress vector and the condition for a jump in the free energy (2.9). Taking into account representation (2.7) of the jump $[\mathbf{F}]$ and the condition (2.1) of the continuity of the temperature θ at the interface, we can write this system in the form

$$\begin{aligned} \mathbf{T}_{\kappa}^{(2)}(\mathbf{F}^{(2)}, \theta) \cdot \mathbf{n}_{\kappa} - \mathbf{F}_{\kappa}(\mathbf{F}, \theta) \cdot \mathbf{n}_{\kappa} &= 0 \\ \psi^{(2)}(\mathbf{F}^{(2)}, \theta) - \psi(\mathbf{F}, \theta) &= \rho_{\kappa}^{-1} \mathbf{h}_{\kappa} \cdot \mathbf{T}_{\kappa} \cdot \mathbf{n}_{\kappa} + \delta_* \end{aligned} \quad (3.1)$$

Here and henceforth $\delta_* = \text{const}$, and the index of the first phase is omitted for brevity. For specified values of \mathbf{F} and \mathbf{n}_κ , relations (3.1) can be regarded as a system of vector and scalar equations for determining the vector \mathbf{h}_κ and the temperature θ . Hence it follows that

$$\theta = \theta(\mathbf{F}, \mathbf{n}_\kappa)$$

This fact determines an important difference between transitions in a solid from phase transitions in an ideal liquid, in which the melting (boiling) point depends only on the pressure and is given by the Clausius–Clapeyron equation [1, 5]

$$d\theta/dp = \theta[V]/Q_\varphi \quad (3.2)$$

where $Q_\varphi = \theta[\eta]$ is the heat of phase transition and $[V]$ is the jump in the specific volume $V = 1/\rho$.

The analogue of Eq. (3.2), which, for a thermoelastic solid, determines the differential characteristics of the dependence of the phase transition temperature on the tensor \mathbf{F} for a fixed normal \mathbf{n}_κ to the interface of the phases, has the form

$$\left\{ [\rho_\kappa \eta] + \mathbf{h}_\kappa \cdot \frac{\partial \mathbf{T}_\kappa}{\partial \theta} \cdot \mathbf{n}_\kappa \right\} \frac{\partial \theta}{\partial \mathbf{F}} = [\mathbf{T}_\kappa] - \mathbf{h}_\kappa \cdot \frac{\partial \mathbf{T}_\kappa}{\partial \mathbf{F}} \cdot \mathbf{n}_\kappa \quad (3.3)$$

To prove the correctness of relation (3.3) we differentiate the second of the equations of system (3.1) with respect to \mathbf{F} with $\mathbf{n}_\kappa = \text{const}$. Taking into account the fact that $\mathbf{h}_\kappa = \mathbf{h}_\kappa(\mathbf{F}, \mathbf{n}_\kappa)$, $\theta = \theta(\mathbf{F}, \mathbf{n}_\kappa)$, we obtained as a result

$$\begin{aligned} & \frac{\partial \Psi^{(2)}}{\partial F_{ij}^{(2)}} \frac{\partial F_{ij}^{(2)}}{\partial F_{ab}^{(2)}} + \frac{\partial \Psi^{(2)}}{\partial \theta} \frac{\partial \theta}{\partial F_{ab}^{(2)}} - \frac{\partial \Psi}{\partial F_{ab}} - \frac{\partial \Psi}{\partial \theta} \frac{\partial \theta}{\partial F_{ab}} = \\ & = \rho_\kappa^{-1} \frac{\partial h_{\kappa i}}{\partial F_{ab}} T_{\kappa ij} n_{\kappa j} + \rho_\kappa^{-1} h_{\kappa i} \left(\frac{\partial T_{\kappa ij}}{\partial F_{ab}} + \frac{\partial T_{\kappa ij}}{\partial \theta} \frac{\partial \theta}{\partial F_{ab}} \right) n_{\kappa j} \end{aligned}$$

If we now use the formulae which relate the stress tensor and the entropy with the free energy of the thermoelastic material

$$\rho_\kappa^{(n)} \frac{\partial \Psi^{(n)}(\mathbf{F}^{(n)}, \theta)}{\partial \mathbf{F}^{(n)}} = \mathbf{T}_\kappa^{(n)}, \quad \frac{\partial \Psi^{(n)}(\mathbf{F}^{(n)}, \theta)}{\partial \theta} = -\eta^{(n)} \quad (3.4)$$

bear in mind condition (2.5) of the continuity of the stress vector, and also the following expression from (2.7)

$$\frac{\partial F_{ij}^{(2)}}{\partial F_{ab}^{(2)}} = \delta_{ia} \delta_{jb} + n_{\kappa j} \frac{\partial h_{\kappa i}}{\partial F_{ab}}$$

we arrive at the required Eq. (3.3)

Another equation, which is a new relation in the theory of phase transitions of a continuum and represents the differential dependence of the phase-transition temperature on the orientation of the interface for a fixed deformation of the initial phase, has the form

$$\left\{ \rho_\kappa [\eta] + \mathbf{h}_\kappa \cdot \frac{\partial \mathbf{T}_\kappa}{\partial \theta} \cdot \mathbf{n}_\kappa \right\} \frac{\partial \theta}{\partial \mathbf{n}_\kappa} = \mathbf{h}_\kappa \cdot [\mathbf{T}_\kappa] \quad (3.5)$$

It can be seen from Eq. (3.5) that the derivate $\partial \theta / \partial \mathbf{n}_\kappa$ is orthogonal to the normal \mathbf{n}_κ , since $\mathbf{h}_\kappa \cdot [\mathbf{T}_\kappa] \cdot \mathbf{n}_\kappa = 0$, by virtue of (2.5).

Equations (3.3) and (3.5) hold for a thermoelastic material with an arbitrary type of anisotropy.

Relation (3.5) is obtained by differentiating the second of the equations of system (3.1) with respect to the vector \mathbf{n}_κ for a fixed value of the tensor \mathbf{F} . Taking formulae (3.4) into account this gives

$$T_{\kappa ij}^{(2)} \frac{\partial F_{ij}^{(2)}}{\partial n_{\kappa a}} + [\rho_\kappa \eta] \frac{\partial \theta}{\partial n_{\kappa a}} = \frac{\partial h_{\kappa i}}{\partial n_{\kappa a}} T_{\kappa ij} n_{\kappa j} + h_{\kappa i} \frac{\partial T_{\kappa ij}}{\partial \theta} \frac{\partial \theta}{\partial n_{\kappa a}} n_{\kappa j} + h_{\kappa i} T_{\kappa ia}$$

The condition of continuity of the stress vector (2.5) and the equation

$$\frac{\partial F_{ij}^{(2)}}{\partial n_{\kappa a}} = h_{\kappa i} \delta_{aj} + n_{\kappa a} \frac{\partial h_{\kappa i}}{\partial n_{\kappa a}}$$

which follows from (2.7), lead to the equation considered.

Consider a thermoelastic material, both phases of which are initially an isotropic material, for which the kinematic phase-transition characteristic U_0 is a spherical tensor. The constitutive relations can be written in the form

$$\begin{aligned} \psi^{(n)} &= \psi^{(n)}(I_k(\mathbf{B}^{(n)}), \theta), \quad \eta^{(n)}(I_k(\mathbf{B}^{(n)}), \theta) = -\frac{\partial \psi^{(n)}(I_k(\mathbf{B}^{(n)}), \theta)}{\partial \theta} \\ \mathbf{T}^{(n)}(\mathbf{B}^{(n)}, \theta) &= \rho^{(n)} \frac{\partial \psi^{(n)}}{\partial \mathbf{F}^{(n)}} \cdot (\mathbf{F}^T)^{(n)} = \beta_0^{(n)} \mathbf{I} + \beta_1^{(n)} \mathbf{B}^{(n)} + \beta_2^{(n)} \mathbf{B}^{(n)} \cdot \mathbf{B}^{(n)} \end{aligned} \quad (3.6)$$

Here β_0 , β_1 and β_2 are scalar functions of the temperature θ and the three independent invariants $I_k(\mathbf{B})$ of the tensor $\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T$, unlike \mathbf{F} , which does not contain a rotation of the material element as a rigid whole.

For the medium considered, Eq. (3.3) reduces to a symmetrical tensor equation for the derivative $\partial\theta/\partial\mathbf{B}$, while relation (3.5) is transformed into an equation for the derivative $\partial\theta/\partial\mathbf{n}$. This assertion becomes obvious if, instead of system (3.1), we consider the condition of continuity of the stress vector (2.12) and relation (2.16) for the jump in energy in Euler variables $\mathbf{x} \in \chi(t)$

$$\begin{aligned} \mathbf{T}^{(2)}(\mathbf{B}^{(2)}, \theta) \cdot \mathbf{n} &= \mathbf{T}(\mathbf{B}, \theta) \cdot \mathbf{n} \\ \psi^{(2)}(\mathbf{B}^{(2)}, \theta) - \psi(\mathbf{B}, \theta) &= \rho_{\kappa}^{-1} \mathbf{h} \cdot \mathbf{T}(\mathbf{B}, \theta) \cdot \mathbf{n} + \delta_* \end{aligned}$$

Hence it follows at once that the phase-transition temperature $\theta = \theta(\mathbf{B}, \mathbf{n})$.

To convert Eqs (3.3) and (3.5) to Euler variables, we will use relations which follow from formulae (2.7) and (2.14)

$$\mathbf{F}^{(2)} = \mathbf{F} + \mathbf{h} \otimes J^{-1} \mathbf{F}^T \cdot \mathbf{n}, \quad \mathbf{h}_{\kappa} = (\rho c / (\rho_{\kappa} c_{\kappa})) \mathbf{h}, \quad \mathbf{n}_{\kappa} = (\rho_{\kappa} c_{\kappa} / (\rho c)) J^{-1} \mathbf{F}^T \cdot \mathbf{n} \quad (3.7)$$

Using these relations and the relation $\mathbf{T}_{\kappa} = J\mathbf{T} \cdot \mathbf{F}^{-1T}$ between the Cauchy and Piola–Kirchhoff stress tensors, Eq. (3.5) can be written in the form

$$J \left\{ [\rho_{\kappa} \eta] + \mathbf{h} \cdot \frac{\partial \mathbf{T}}{\partial \theta} \cdot \mathbf{n} \right\} \frac{\partial \theta}{\partial \mathbf{n}} = \mathbf{h} \cdot [J\mathbf{T} \cdot \mathbf{F}^{-1T}] \cdot \mathbf{F}^T$$

Using formulae (2.12) and (2.14) we convert the right-hand side of this equation as follows:

$$\begin{aligned} [J\mathbf{T} \cdot \mathbf{F}^{-1T}] \cdot \mathbf{F}^T &= (J\mathbf{T} \cdot \mathbf{F}^{-1T})^{(2)} \cdot (\mathbf{F}^T)^{(2)} - \\ &- (J\mathbf{T} \cdot \mathbf{F}^{-1T})^{(2)} \cdot (J^{-1} \mathbf{F}^T \cdot \mathbf{n})^{(2)} \otimes \mathbf{h} - J\mathbf{T} \cdot \mathbf{F}^{-1T} \cdot \mathbf{F}^T = [J\mathbf{T}] - \mathbf{T} \cdot \mathbf{n} \otimes \mathbf{h} \end{aligned} \quad (3.8)$$

which finally gives

$$J \left\{ [\rho_{\kappa} \eta] + \mathbf{h} \cdot \frac{\partial \mathbf{T}}{\partial \theta} \cdot \mathbf{n} \right\} \frac{\partial \theta}{\partial \mathbf{n}} = [J\mathbf{T}] \cdot \mathbf{h} - (\mathbf{h} \cdot \mathbf{T} \cdot \mathbf{n}) \mathbf{h} \quad (3.9)$$

If both phase are liquid, for which

$$\mathbf{T} = -p(V, \theta) \mathbf{I}, \quad V = J/\rho_{\kappa} = 1/\rho$$

the derivative $\partial\theta/\partial\mathbf{n}$ is identically equal to zero.

In fact, in this case, taking into account the continuity of the pressure at the interface, the right-hand side of Eq. (3.9) can be written in the form $p(\mathbf{h} \cdot \mathbf{n} - [V])\mathbf{h}$. This quantity is equal to zero, since it follows from relation (2.11) that

$$[V] = [\rho^{-1}] = [c]/(\rho c) = -[\mathbf{v}] \cdot \mathbf{n}/(\rho c)$$

Bearing in mind definition (2.14) of the vector \mathbf{h} , we obtain

$$\mathbf{h} \cdot \mathbf{n} = \rho_\kappa [V] = [J] \quad (3.10)$$

Hence the required assertion immediately follows.

When both phases are solid, there is an orientation of the interface which yields an extremum of the phase-transition temperature for a fixed state of the initial phase. This extremum value occurs in the case when one of the principal axes of the finite-deformation tensor \mathbf{B} coincides with the normal \mathbf{n} to the interface.

In fact, suppose

$$\mathbf{B} = B_0 \mathbf{n} \otimes \mathbf{n} + B_{\alpha\beta} \mathbf{e}_\alpha \otimes \mathbf{e}_\beta, \quad \alpha, \beta = 1, 2 \quad (3.11)$$

where \mathbf{e}_α are the unit vectors of the principal axes of the tensor \mathbf{B} , which lie in a plane tangential to the interface. By virtue of the polynomial representation (3.10), the Cauchy stress tensor in the initially isotropic medium will have the same structure

$$\mathbf{T} = T_0 \mathbf{n} \otimes \mathbf{n} + T_{\alpha\beta} \mathbf{e}_\alpha \otimes \mathbf{e}_\beta, \quad \alpha, \beta = 1, 2 \quad (3.12)$$

It follows from the condition of continuity of the stress tensor (2.12) that

$$\mathbf{T}^{(2)} = T_0 \mathbf{n} \otimes \mathbf{n} + T_{\alpha\beta}^{(2)} \mathbf{e}_\alpha \otimes \mathbf{e}_\beta$$

For a material with a one-to-one correspondence between the tensor $\mathbf{T}^{(2)}$ and $\mathbf{B}^{(2)}$ we have

$$\mathbf{B}^{(2)} = B_0^{(2)} \mathbf{n} \otimes \mathbf{n} + B_{\alpha\beta}^{(2)} \mathbf{e}_\alpha \otimes \mathbf{e}_\beta$$

This indicates that

$$[\mathbf{B}] = [B_0] \mathbf{n} \otimes \mathbf{n} + [B_{\alpha\beta}] \mathbf{e}_\alpha \otimes \mathbf{e}_\beta \quad (3.13)$$

We will now turn to the first relation of (3.11), from which, for the deformed state considered, it follows that

$$[\mathbf{B}] = \mathbf{b} \otimes \mathbf{h} + \mathbf{h} \otimes \mathbf{b} + (\mathbf{b} \cdot \mathbf{b}) \mathbf{h} \otimes \mathbf{h}, \quad \mathbf{b} = \mathcal{J}^{-1} \mathbf{B} \cdot \mathbf{n} = b \mathbf{n}, \quad b = \mathcal{J}^{-1} B_0$$

Representing the vector \mathbf{h} in the form of the sum normal and tangential components

$$\mathbf{h} = h_n \mathbf{n} + h_\alpha \mathbf{e}_\alpha, \quad h_n = \mathbf{h} \cdot \mathbf{n}, \quad h_\alpha = \mathbf{h} \cdot \mathbf{e}_\alpha, \quad \alpha = 1, 2$$

and substituting into the previous relation, we obtain

$$[\mathbf{B}] = b h_n (2 + b h_n) \mathbf{n} \otimes \mathbf{n} + b (1 + b h_n) h_\alpha (\mathbf{n} \otimes \mathbf{e}_\alpha + \mathbf{e}_\alpha \otimes \mathbf{n}) + b^2 h_\alpha h_\beta \mathbf{e}_\alpha \otimes \mathbf{e}_\beta$$

Comparing this formula with relation (3.13), we see that $\mathbf{h} = h_n \mathbf{n}$. Hence, taking relation (3.10) into account, it follows that $[B_{\alpha\beta}] = 0$, i.e. all the components of the tensor \mathbf{B} , with the exception of the normal component B_0 , are continuous on the interface. We emphasise that the continuity of the components $B_{\alpha\beta}$ is satisfied for state (3.11), but in general this continuity does not occur.

Substituting the vector $\mathbf{h} = h_n \mathbf{n}$ into relation (3.9) we obtain that the derivative $\partial\theta/\partial\mathbf{n}$ equal to zero, which corresponds to an extremum of the phase-transition temperature for deformed state (3.11).

If one of the phases is a liquid, the deformation tensor may be reduced, by a unimodular transformation of the reference configuration, to the form (3.11). This means that, for a “solid-liquid” phase transition, we can assume, without loss of generality, that $\mathbf{h} = h_n \mathbf{n}$, which leads to the condition $\partial\theta/\partial\mathbf{n} = 0$. Hence it immediately follows that the phase-transition temperature is independent of the orientation of the interface, if one of the phases at the elastic initially isotropic material is liquid. This assertion to some extent justifies the applicability of classical theory to describe the melting (evaporation) of solids and shows that a consideration of solid effects does not change the cardinal picture of this process.

The equation which determines the dependence of the phase-transition temperature on the finite-deformation tensor of the initial phase, has the form

$$2 \left\{ [\rho_\kappa \eta] + \mathbf{h} \cdot \frac{\partial \mathbf{T}}{\partial \theta} \cdot \mathbf{n} \right\} \frac{\partial \theta}{\partial \mathbf{B}} \cdot \mathbf{B} = (\mathbf{I} + \mathbf{n} \otimes J^{-1} \mathbf{h}) \cdot ([J\mathbf{T}] - (\mathbf{h} \cdot \mathbf{T} \cdot \mathbf{n}) \mathbf{I}) + \quad (3.14)$$

$$+ \{ \mathbf{n} \otimes \mathbf{h} \cdot \mathbf{T} - \mathbf{T} \cdot \mathbf{n} \otimes \mathbf{h} \} - 2(\mathbf{n} \otimes \mathbf{h}) : \mathbf{L} \cdot \mathbf{B}$$

where $\mathbf{L} = \partial \mathbf{T} / \partial \mathbf{B}$ is a fourth-rank tensor of the elastic coefficients.

To derive this equation we turn to Eq. (3.3). Using relations (3.6) and the relation $\mathbf{T}_\kappa = J\mathbf{T} \cdot \mathbf{F}^{-1T}$ between the stress tensors, we obtain, after substitution into Eq. (3.3).

$$\left\{ [\rho_\kappa \eta] + \mathbf{h} \cdot \frac{\partial \mathbf{T}}{\partial \theta} \cdot \mathbf{n} \right\} \frac{\partial \theta}{\partial \mathbf{F}} \Big|_{\mathbf{n}_\kappa} = [J\mathbf{T} \cdot \mathbf{F}^{-1T}] - J^{-1} \mathbf{h} \otimes \mathbf{F}^T \cdot \mathbf{n} : \frac{\partial (J\mathbf{T} \cdot \mathbf{F}^{-1T})}{\partial \mathbf{F}} \quad (3.15)$$

The derivative of the phase-transition temperature with respect to the tensor \mathbf{F} for a fixed normal \mathbf{n}_κ is

$$\frac{\partial \theta(\mathbf{B}, \mathbf{n}(\mathbf{F}, \mathbf{n}_\kappa))}{\partial F_{ab}} \Big|_{\mathbf{n}_\kappa} = \frac{\partial \theta}{\partial B_{ij}} \Big|_n \frac{\partial B_{ij}}{\partial F_{ab}} + \frac{\partial \theta}{\partial n_i} \Big|_B \frac{\partial n_i}{\partial F_{ab}} = 2 \frac{\partial \theta}{\partial B_{aj}} \Big|_n F_{jb} - n_a \frac{\partial \theta}{\partial n_i} \Big|_B F_{ib}^{-1T}$$

Here we have used the formula $\partial F_{is}^{-1T} / \partial F_{ab} = -F_{ib}^{-1T} F_{as}^{-1T}$, which is obtained by differentiating the identity $F_{si}^{-1} F_{ik} = \delta_{yk}$ with respect to F_{ab} . Substituting this relation into (3.15) we obtain the equation

$$2 \left\{ [\rho_\kappa \eta] + \mathbf{h} \cdot \frac{\partial \mathbf{T}}{\partial \theta} \cdot \mathbf{n} \right\} \frac{\partial \theta}{\partial \mathbf{B}} \Big|_n \cdot \mathbf{F} = (\mathbf{I} + \mathbf{n} \otimes J^{-1} \mathbf{h}) [J\mathbf{T} \cdot \mathbf{F}^{-1T}] - (\mathbf{h} \otimes J^{-1} \mathbf{F}^T \cdot \mathbf{n}) : \frac{\partial (J\mathbf{T} \cdot \mathbf{F}^{-1T})}{\partial \mathbf{F}}$$

Expanding the derivative in the last term, taking into account the formulae

$$\frac{\partial J}{\partial \mathbf{F}} = J\mathbf{F}^{-1T}, \quad \frac{\partial F_{is}^{-1T}}{\partial F_{ab}} = -F_{ib}^{-1T} F_{as}^{-1T}, \quad \frac{\partial T_{ik}}{\partial F_{ab}} = 2 \frac{\partial T_{ik}}{\partial B_{am}} F_{mb}$$

and multiplying the equation scalarly on the right by \mathbf{F}^T , we obtain

$$2 \left\{ [\rho_\kappa \eta] + \mathbf{h} \cdot \frac{\partial \mathbf{T}}{\partial \theta} \cdot \mathbf{n} \right\} \frac{\partial \theta}{\partial \mathbf{B}} \cdot \mathbf{B} =$$

$$= (\mathbf{I} + \mathbf{n} \otimes J^{-1} \mathbf{h}) \cdot [J\mathbf{T} \cdot \mathbf{F}^{-1T}] \cdot \mathbf{F}^T - (\mathbf{h} \cdot \mathbf{T} \cdot \mathbf{n}) \mathbf{I} + \mathbf{n} \otimes J^{-1} \mathbf{h} \cdot \mathbf{T} + 2(\mathbf{h} \otimes \mathbf{n}) : \mathbf{L} \cdot \mathbf{B}$$

Using formula (3.8) and reducing like terms, we obtain the required Eq. (3.14).

For the deformed state (3.11), for which there are no shear strains (shear stresses) at the interface, Eq. (3.14) can be reduced to two simpler relations

$$\left([\eta] + [V] \frac{\partial T_0}{\partial \theta} \right) \frac{\partial \theta}{\partial B_0} = -[V] \frac{\partial T_0}{\partial B_0} \quad (3.16)$$

$$\left([\eta] + [V] \frac{\partial T_0}{\partial \theta} \right) \frac{\partial \theta}{\partial B_{\alpha\beta}} = \frac{1}{2} [V(T_{\alpha\gamma} - T_0 \delta_{\alpha\gamma})] B_{\gamma\beta}^{-1} - [V] \beta_{ij} B_0' B_{\alpha\beta}' \quad (3.17)$$

Formula (3.16) was obtained previously in [8] for the case when one of the phases is a liquid.

To derive relations (3.16) and (3.17) we note that, by virtue of formulae (3.12) and (3.13),

$$[J\mathbf{T}] = [J]T_0 \mathbf{n} \otimes \mathbf{n} + [JT_{\alpha\beta}] \mathbf{e}_\alpha \otimes \mathbf{e}_\beta, \quad \mathbf{e}_\alpha \cdot \mathbf{n} = 0, \quad \alpha, \beta = 1, 2$$

Taking into account the fact that, for the deformation considered $\mathbf{h} = [J]\mathbf{n}$, we obtain $\mathbf{h} \cdot \mathbf{T} \cdot \mathbf{n} = [J]T_0$. Hence it follows that the first term on the right-hand side of (3.14) is equal to

$$[J(T_{\alpha\beta} - \delta_{\alpha\beta}T_0)]\mathbf{e}_\alpha \otimes \mathbf{e}_\beta, \quad \alpha, \beta = 1, 2$$

while the second term, by virtue of formula (3.11) and the colinearity of the vectors \mathbf{h} and \mathbf{n} , vanishes. The last term is equal to

$$-2[J]\{(\beta_1 + 2\beta_2 B_0 + \beta_{AB} B_0^{A+B})\mathbf{n} \otimes \mathbf{n} + \beta_{AB} B_0^A B_{\alpha\beta}^B \mathbf{e}_\alpha \otimes \mathbf{e}_\beta\} \cdot \mathbf{B}, \quad A, B = 0, 1, 2$$

where

$$\beta_{A0} = \left(\frac{\partial}{\partial I_1} + I_1 \frac{\partial}{\partial I_2} + I_2 \frac{\partial}{\partial I_3} \right) \beta_A, \quad \beta_{A1} = - \left(\frac{\partial}{\partial I_2} + I_1 \frac{\partial}{\partial I_3} \right) \beta_A, \quad \beta_{A2} = \frac{\partial \beta_A}{\partial I_3}$$

These expressions can be obtained by differentiating the polynomial representation (3.6) of the Cauchy stress tensor, taking into account the definition of the principal invariants $I_k(\mathbf{B})$ and the Hamilton–Cayley theorem

$$\begin{aligned} \frac{\partial \mathbf{T}}{\partial \mathbf{B}} &= \mathbf{B}^A \otimes \frac{\partial \beta_A}{\partial \mathbf{B}} + \beta_1 \frac{\partial \mathbf{B}}{\partial \mathbf{B}} + \beta_2 \frac{\partial(\mathbf{B}\mathbf{B})}{\partial \mathbf{B}} = \\ &= \beta_{AB} \mathbf{B}^A \otimes \mathbf{B}^B + \beta_1 \mathbf{1} + \beta_2 (\mathbf{I} \otimes \mathbf{B}^{(1342)} + \mathbf{I} \otimes \mathbf{B}^{(1432)} + \mathbf{I} \otimes \mathbf{B}^{(2413)} + \mathbf{I} \otimes \mathbf{B}^{(2314)}) \end{aligned}$$

where $\mathbf{1} = \frac{1}{2}(\delta_{ia}\delta_{jb} + \delta_{ib}\delta_{ja})\mathbf{e}^i \otimes \mathbf{e}^j \otimes \mathbf{e}^a \otimes \mathbf{e}^b$ is a fourth-rank unit tensor, while $\mathbf{I} \otimes \mathbf{B}^{(1342)} = \delta_{ia}B_{bj}\mathbf{e}^i \otimes \mathbf{e}^j \otimes \mathbf{e}^a \otimes \mathbf{e}^b$ is the isomer of the tensor $\mathbf{I} \otimes \mathbf{B}$. Since the quantity $(\beta_1 + 2\beta_2 B_0 + \beta_{AB} B_0^{A+B})$ is equal to $\partial T_0 / \partial B_0$, relations (3.16) and (3.17) are proved.

4. A LINER INITIALLY ISOTROPIC THERMOELASTIC MATERIAL

We will consider, as an illustration, a phase transition of the first kind in a linear initially isotropic thermoelastic solid, which is of independent interest. We will use as the initial configuration κ of each of the phases a configuration with the same temperature θ_0 and the same density ρ_κ . The initial state of the first phase will be assumed to be natural (unstressed), and the second phase in configuration κ is characterized by an initial stress $\mathbf{T} = -p_0 \mathbf{I}$. The deformations of each of the phases, measured from the configuration κ , are assumed to be small. The singular source of entropy is assumed to be constant. The free energy density of each of the phases is taken in the form

$$\begin{aligned} \rho_\kappa \Psi^{(n)} &= \rho_\kappa \psi_\kappa^{(n)} - \rho_\kappa \eta_\kappa^{(n)} \vartheta - p_\kappa^{(n)} I_1^{(n)} + \\ &+ \frac{1}{2} \lambda^{(n)} (I_1^{(n)})^2 + \mu^{(n)} (\mathbf{e} : \mathbf{e})^{(n)} - \alpha^{(n)} I_1^{(n)} \vartheta - \frac{1}{2\theta_0} c^{(n)} \vartheta^2 \end{aligned} \quad (4.1)$$

when $n = 1, 2$ is the number of the phase, \mathbf{e} is the small deformation tensor, $I_1 = \mathbf{I} : \mathbf{e}$, $\vartheta = \theta - \theta_0$, $\vartheta/\theta_0 \ll 1$, and the coefficients $\psi_\kappa^{(n)}$, $p_\kappa^{(n)}$, $\eta_\kappa^{(n)}$, $c^{(n)}$, $\alpha^{(n)}$, $\lambda^{(n)}$, $\mu^{(n)}$ are functions of the temperature θ_0 . The entropy density and the stress tensor in each material are written as follows:

$$\begin{aligned} \rho_\kappa \eta^{(n)} &= \rho_\kappa \eta_\kappa^{(n)} + \alpha^{(n)} I_1^{(n)} + c^{(n)} \vartheta / \theta_0 \\ \mathbf{T}^{(n)} &= (\lambda^{(n)} I_1^{(n)} - p_\kappa^{(n)} - \alpha^{(n)} \vartheta) \mathbf{I} + 2\mu^{(n)} \mathbf{e}^{(n)} \end{aligned} \quad (4.2)$$

Hence it can be seen that $\lambda^{(n)}$, $\mu^{(n)}$ are Lamé coefficients, $\alpha^{(n)}$ is the coefficient of thermal expansion, $c^{(n)}$ is the heat capacity, while the quantities $\psi_\kappa^{(n)}$, $\eta_\kappa^{(n)}$ characterize the free energy and entropy of the phases in the initial states. We will assume that

$$\psi_\kappa^{(1)} = 0, \quad \psi_\kappa^{(2)} = \psi_0, \quad \eta_\kappa^{(1)} = 0, \quad \eta_\kappa^{(2)} = \eta_0$$

As already pointed out, $p_\kappa^{(1)} = 0$, $p_\kappa^{(2)} = p_0$. It follows from relations (4.2) that the approximation of small deformations, measured from the configuration κ , holds if the initial pressure p_0 is small compared with the moduli of elasticity.

The assumption that the deformations of each of the phases are small, implies smallness of the jump, which experiences a rotation of a material particle on the phase boundary.

In fact, suppose the tensor \mathbf{F} has the form

$$\mathbf{F} = \mathbf{R} \cdot \mathbf{U} = \mathbf{R} \cdot (\mathbf{I} + \mathbf{e}_\kappa)$$

where \mathbf{e}_κ is the small-deformation tensor, which is of the order of δ , where $\delta \ll 1$ is a small parameter, while \mathbf{R} is the orthogonal tensor of finite rotation. Then, apart from terms $O(\delta^2)$, the quantity

$$\mathbf{F} \cdot \mathbf{F}^T = \mathbf{R} \cdot (\mathbf{I} + 2\mathbf{e}_\kappa) \cdot \mathbf{R}^T = 2\mathbf{e} + \mathbf{I}$$

where $\mathbf{e} = \mathbf{R} \cdot \mathbf{e}_\kappa \cdot \mathbf{R}^T$ is the deformation tensor, which, like \mathbf{e}_κ is of the order of δ . Using the formula $[ab] = a[b] + [a]b + [a][b]$ and relation (2.14), we obtain

$$\begin{aligned} 2[\mathbf{e}] &= [\mathbf{F}] \cdot \mathbf{F}^T + \mathbf{F} \cdot [\mathbf{F}^T] + [\mathbf{F}] \cdot [\mathbf{F}^T] = \\ &= J^{-1} \mathbf{h} \otimes \mathbf{n} \cdot \mathbf{F} \cdot \mathbf{F}^T + J^{-1} \mathbf{F} \cdot \mathbf{F}^T \cdot \mathbf{n} + J^{-2} (\mathbf{h} \otimes \mathbf{h}) \mathbf{n} \cdot \mathbf{F} \cdot \mathbf{F}^T \cdot \mathbf{n} \end{aligned}$$

Taking into account the fact that $J = \det \mathbf{F} = 1 + I_1(\mathbf{e}) + O(\delta^2)$ and $\mathbf{F} \cdot \mathbf{F}^T = 2\mathbf{e} - \mathbf{I}$, the relation obtained can be reduced to the form

$$\begin{aligned} 2[\mathbf{e}] &= \{2\mathbf{h} \otimes \mathbf{e} \cdot \mathbf{n} + 2\mathbf{e} \cdot \mathbf{n} \otimes \mathbf{h} + 2(\mathbf{n} \cdot \mathbf{e} \cdot \mathbf{n}) \mathbf{h} \otimes \mathbf{h}\} + \\ &+ I_1(\mathbf{h} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{h} + 2\mathbf{h} \otimes \mathbf{h}) - (\mathbf{h} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{h} + \mathbf{h} \otimes \mathbf{h}) + O(\delta^2) \end{aligned}$$

Since the left-hand side and the first two terms on the right-hand side are of the order of δ , the third term on the right-hand side must have the same order, i.e.

$$\mathbf{h} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{h} + \mathbf{h} \otimes \mathbf{h} = O(\delta)$$

Hence we have the relations

$$\mathbf{h} + (\mathbf{h} \cdot \mathbf{n}) \mathbf{n} + (\mathbf{h} \cdot \mathbf{n}) \mathbf{h} = O(\delta), \quad 2(\mathbf{h} \cdot \mathbf{n}) + (\mathbf{h} \cdot \mathbf{n})^2 = O(\delta)$$

The second equation has the solutions $(\mathbf{h} \cdot \mathbf{n}) = O(\delta)$ and $(\mathbf{h} \cdot \mathbf{n}) = -2 + O(\delta)$. Substituting $(\mathbf{h} \cdot \mathbf{n}) = O(\delta)$ into the first equation we obtain $\mathbf{h} = O(\delta)$, which corresponds to a small jump in the rotation of a material element on the phase boundary. The solution $(\mathbf{h} \cdot \mathbf{n}) = -2 + O(\delta)$ describes a finite jump of rotation. However, this solution is inapplicable since, from the formula $[J^{-1} \mathbf{F}^T] \cdot \mathbf{n} = 0$, which is obtained from the Piola identity $\nabla \cdot (J^{-1} \mathbf{F}) = 0$, taking into account the relation $J = 1 + O(\delta)$, it follows that $[\mathbf{F}^T] \cdot \mathbf{n} = O(\delta)$. Hence we obtain $(\mathbf{h} \cdot \mathbf{n}) \mathbf{F}^T \cdot \mathbf{n} = O(\delta)$. The vector $\mathbf{F}^T \cdot \mathbf{n}$ is not identically equal to zero, since in the opposite case we would have a non-trivial solution of a uniform non-degenerate linear system $\mathbf{F}^T \cdot \mathbf{n} = 0$, $\det \mathbf{F} \neq 0$. This denotes that $(\mathbf{h} \cdot \mathbf{n}) = O(\delta)$.

Note that the result obtained holds for a material with an arbitrary type of symmetry. It can be applied to the process of recrystallization, which is a special case of a phase transition of anisotropic solids, when the initial and product phases are one and the same material. The elements of the material on passing through the interface undergo deformation and rotation, leading to a change in the spatial orientation of the anisotropy axes. Since the smallness of the deformations implies smallness of the rotations, we can assert that recrystallization is a particularly non-linear phenomenon, which is necessarily accompanied by a finite deformation.

Taking the above relations into account, we can write the jump in the stress tensor in the form

$$\begin{aligned} [\mathbf{T}] &= \{\lambda^{(2)}(\mathbf{h} \cdot \mathbf{n}) + \Lambda \sigma_0\} \mathbf{I} + \mu^{(2)}(\mathbf{h} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{h}) + 2\mu_* \Lambda \mathbf{e} \\ \lambda_* &= [\lambda]/\Lambda, \quad \mu_* = [\mu]/\Lambda, \quad p_* = p_0/\Lambda, \quad \alpha_* = [\alpha]/\Lambda \end{aligned} \quad (4.3)$$

$$\Lambda = \lambda^{(2)} + 2\mu^{(2)}, \quad \sigma_0 = \lambda_* I_1 - p_* - \alpha_* \vartheta$$

The relation between the vectors \mathbf{n} , \mathbf{h} and $\mathbf{e} \cdot \mathbf{n}$

$$\mu^{(2)} \mathbf{h} + \{(\lambda^{(2)} + \mu^{(2)})(\mathbf{h} \cdot \mathbf{n}) + \Lambda \sigma_0\} \mathbf{n} + 2\mu_* \Lambda \mathbf{e} \cdot \mathbf{n} = 0 \quad (4.4)$$

follows from formula (4.3) and the condition $[\mathbf{T}] \cdot \mathbf{n} = 0$. Hence

$$\begin{aligned} \mathbf{h} &= -(\sigma_0 + 2\mu_* \mathbf{n} \cdot \mathbf{e} \cdot \mathbf{n}) \mathbf{n} - 2\mu_* \Lambda \mathbf{m} \\ l &= \Lambda/\mu^{(2)}, \quad \mathbf{m} = \{\mathbf{I} - \mathbf{n} \otimes \mathbf{n}\} \cdot \mathbf{e} \cdot \mathbf{n}, \quad \mathbf{m} \cdot \mathbf{n} = 0 \end{aligned} \quad (4.5)$$

where \mathbf{m} is the component of the vector $\mathbf{e} \cdot \mathbf{n}$ tangential to the interface. It follows from relations (4.5) that

$$\begin{aligned} \mathbf{h} \cdot \mathbf{h} &= (\sigma_0 + 2\mu_* \mathbf{n} \cdot \mathbf{e} \cdot \mathbf{n})^2 + 4\mu_*^2 l^2 \mathbf{m} \cdot \mathbf{m} = (\sigma_0 + 2\mu_* \mathbf{n} \cdot \mathbf{e} \cdot \mathbf{n})^2 + 4\mu_*^2 l^2 ((\mathbf{e} \cdot \mathbf{n}) \times \mathbf{n})^2 \\ \mathbf{m} \cdot \mathbf{m} &= (\mathbf{e} \cdot \mathbf{n}) \cdot \{\mathbf{I} - \mathbf{n} \otimes \mathbf{n}\}^2 \cdot (\mathbf{e} \cdot \mathbf{n}) = (\mathbf{n} \cdot \mathbf{e}^2 \cdot \mathbf{n}) - (\mathbf{n} \cdot \mathbf{e} \cdot \mathbf{n})^2 = ((\mathbf{e} \cdot \mathbf{n}) \times \mathbf{n})^2 \end{aligned} \quad (4.6)$$

We will now turn to relation (2.16), which can be written in the form

$$[\rho_\kappa \Psi] = \mathbf{h} \cdot \mathbf{T}^{(2)} \cdot \mathbf{n} + \rho_\kappa \delta_* \quad (4.7)$$

Taking into account the relations

$$\begin{aligned} [I_1^2] &= 2I_1^{(2)} \mathbf{h} \cdot \mathbf{n} - (\mathbf{h} \cdot \mathbf{n})^2, \quad [\mathbf{e} : \mathbf{e}] = 2(\mathbf{h} \cdot \mathbf{e} \cdot \mathbf{n}) + 1/2((\mathbf{h} \cdot \mathbf{h}) + (\mathbf{h} \cdot \mathbf{n})^2) \\ p_0 I_1^{(2)} &= p_0 I_1 + p_0 (\mathbf{h} \cdot \mathbf{n}), \quad 1/2[\lambda I_1^2] = \lambda^{(2)} I_1^{(2)} (\mathbf{h} \cdot \mathbf{n}) - 1/2 \lambda^{(2)} (\mathbf{h} \cdot \mathbf{n})^2 + 1/2 [\lambda] I_1^2 \\ [\mu \mathbf{e} : \mathbf{e}] &= 2\mu^{(2)} (\mathbf{h} \cdot \mathbf{e} \cdot \mathbf{n}) + 1/2 \mu^{(2)} (\mathbf{h} \cdot \mathbf{h}) + 1/2 \mu^{(2)} (\mathbf{h} \cdot \mathbf{n})^2 + [\mu] \mathbf{e} : \mathbf{e} \\ [\alpha I_1] \vartheta &= \alpha^{(2)} \vartheta (\mathbf{h} \cdot \mathbf{n}) + [\alpha] I_1 \vartheta \end{aligned}$$

and formulae (4.3), (4.5) and (4.6), Eq. (4.7) can be reduced to the form

$$\begin{aligned} \Psi_* - \eta_* \bar{\vartheta} - p_* I_1 + \frac{1}{2} \lambda_* I_1^2 + \mu_* \mathbf{e} : \mathbf{e} - \alpha_* I_1 \bar{\vartheta} - \frac{1}{2} c_* \bar{\vartheta}^2 &= \frac{1}{2} (\mathbf{h} \cdot \mathbf{n})^2 + 2\mu_*^2 l (\mathbf{m} \cdot \mathbf{m}) \\ \bar{\vartheta} \equiv \vartheta / \theta_0, \quad \Psi_* \equiv \rho_\kappa (\Psi_0 - \delta_*) / \Lambda, \quad \eta_* \equiv \rho_\kappa \eta_0 \theta_0 / \Lambda, \quad c_* \equiv [c] \theta_0 / \Lambda \end{aligned} \quad (4.8)$$

From Eq. (4.8), taking expression (4.5) for the vector \mathbf{h} into account, it follows that when the dimensionless jump in entropy $\eta_* = O(1)$, the phase-transition temperature

$$\bar{\vartheta} = \Psi_* / \eta_* + O(\delta^2) \quad (4.9)$$

i.e. only the energy characteristics of the phase transition Ψ_* and η_* and of the dissipation δ_* , which accompany the change in the structure of the material, are determined. It makes no sense to take into account terms $O(\delta^2)$ in the approximation considered since Eqs (4.2) are written up to terms of first order infinitesimals.

When $\eta_* = O(\delta)$, the phase-transition temperature depends very much on the strain tensor of the initial phase and the orientation of the normal to the interface with respect to the principal axes of the tensor \mathbf{e} . Before we investigate this relation, we note that the difference in the thermoelastic coefficients of the phases of the material, generally speaking, may be quite high [29]. Hence, we will consider the case when

$$\lambda_* = O(1), \quad \mu_* = O(1), \quad \alpha_* = O(1), \quad c_* = O(1), \quad p_* = O(\delta)$$

The equation of the derivative of the phase-transition temperature with respect to the vector of the normal in this approximation is written in the form

$$M \Lambda \partial \bar{\vartheta} / \partial \mathbf{n} = [\mathbf{T}] \cdot \mathbf{h}, \quad M \equiv \eta_* + \alpha_* I_1 + c_* \bar{\vartheta} + \alpha_* (\mathbf{h} \cdot \mathbf{n})$$

Bearing expressions (4.3) and (4.5) in mind and taking into account the continuity of the stress vector, the relation obtained can be converted to the form

$$M \partial \bar{\vartheta} / \partial \mathbf{n} = -4\mu_* (\sigma_0 + 2\mu_* e_0) \mathbf{m} - 4\mu_*^2 l (\mathbf{e} \cdot \mathbf{m} - e_0 \mathbf{m} - (\mathbf{m} \cdot \mathbf{m}) \mathbf{n}) \quad (4.10)$$

The normal, which coincides with the principal axis of the small-deformation tensor of the initial phase

$$\mathbf{e} = e_0 \mathbf{n} \otimes \mathbf{n} + e_{\alpha\beta} \mathbf{e}_\alpha \otimes \mathbf{e}_\beta \quad (4.11)$$

yields an extremum of the phase-transition temperature, since in such a deformation the vector $\mathbf{m} = 0$ and, consequently, $\partial\bar{\vartheta}/\partial\mathbf{n} = 0$. The form of the extremum is determined by the matrix $\partial^2\bar{\vartheta}/\partial\mathbf{n} \otimes \partial\mathbf{n} = 0$ for deformation (4.11).

Taking expressions (4.3) and (4.5) into account, the equation for the derivative of the phase-transition temperature with respect to the deformation tensor can be written in the form

$$M\Lambda\partial\bar{\vartheta}/\partial\mathbf{e} = [\mathbf{T}] - \mathbf{h} \cdot (\partial\mathbf{T}/\partial\mathbf{e}) \cdot \mathbf{n} \quad (4.12)$$

It follows from Eq. (4.12) that for bulk deformation of the initial phase, the type of the phase transition in a linear thermoelastic solid with the rheological characteristic $\eta_* = O(\delta)$ inevitably changes, i.e. the normal (anomalous) phase transition changes into an anomalous (normal) transition.

In fact, for a fixed normal and a constant intensity of the shear strain $I_2 = (\mathbf{e}' : \mathbf{e}')^{1/2} = \text{const}$, where $\mathbf{e}' = \mathbf{e} - 1/3I_1\mathbf{I}$ is the deviator of the strain tensor, the derivative of the phase-transition temperature with respect to the first invariant is equal to

$$M\partial\bar{\vartheta}/\partial I_1 = (1 - K_*)(K_*I_1 - p_* - \alpha_*\bar{\vartheta}) - 2\mu_*K_*\mathbf{n} \cdot \mathbf{e}' \cdot \mathbf{n}, \quad K_* = \lambda_* + 2\mu_*/3 \quad (4.13)$$

The right-hand side of relation (4.13) vanishes if the normal to the phase boundary of the component of the strain tensor is related to the other two diagonal components by the relation

$$K_*(e_{11} + e_{22} + e_{33}) - p_* - \alpha_*\bar{\vartheta}(\mathbf{e}, \mathbf{n}) = \frac{2\mu_*K_*}{1 - K_*} \left(\frac{2}{3}e_{11} - \frac{1}{3}(e_{22} + e_{33}) \right)$$

The strain tensor yields an extremum with respect to I_1 of the phase-transition temperature. With $\alpha_* = O(\delta)$, this relation, apart from second-order infinitesimals, can be written in the explicit form

$$e_{11} = \frac{p_*}{K_*} \frac{1 - K_*}{1 - \Lambda_*} - \frac{1 - \lambda_*}{1 - \Lambda_*} (e_{22} + e_{33}), \quad \Lambda_* = \lambda_* + 2\mu_* \quad (4.14)$$

In the case of spherical tension (compression), when the deviator \mathbf{e}' is equal to zero, this relation becomes particularly simple and has the form

$$e_{11} = e_{22} = e_{33} = p_*/(3K_*)$$

In the general case, the deformations, which yield an extremum to the phase-transition temperature, are defined by the solution of the system which consists of Eq. (4.14) and the condition $\mathbf{e}' : \mathbf{e}' = \text{const}$ of constant intensity of shear deformation.

As in the case of an ideal liquid, we will say that a phase transition is normal if an increase in the bulk deformation leads to a reduction in the phase-transition temperature ($\partial\bar{\vartheta}/\partial I_1 < 0$). Otherwise, the phase transition is anomalous, and the reduction in the temperature of the phase transition ($\partial\bar{\vartheta}/\partial I_1 > 0$) in this material occurs for compression deformation. The existence of this extremum indicates that, for sufficiently large changes in the bulk deformation of the initial phase the type of the transition in the material considered necessarily changes, and a transition occurs from a normal phase change to an anomalous one (or vice versa). This occurs provided the phase transition is accompanied by a change in the moduli of elasticity, compared with the value of the moduli themselves, while the jump in entropy is small in the sense indicated above. The existence of this effect is due purely to the solid-state properties of the material – the presence of a stress deviator and its effect on the energy of the equilibrium state of the medium.

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