Thermodynamics of Coherent Phase Transformations in Nonhydrostatically Stressed Solids

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Abstract—It is shown that in diffusionless coherent first-order phase transformations in stressed solids an energy-momentum tensor appears in the role of a chemical potential. A thermodynamic equilibrium condition is derived in terms of this tensor from balance relations and a dissipation inequality, and its use in formulating linear phenomenological relations for irreversible phase transformations in non-hydrostatic systems is pointed out.

Key words: Coherent phase transformation; Nonhydrostatic thermodynamics.

1. Introduction

The thermodynamic theory of diffusionless coherent first-order phase transformations in stressed solids is fundamental to many problems in such fields as physical chemistry and metallurgy, and has been dealt with, and debated especially, in the geophysical and geological literature (KAMB, 1959, 1961; COE and PATERSON, 1969; IDA, 1969; FLETCHER, 1973; PATERSON, 1973; ROBIN, 1974; MCLELLAN, 1970, 1980). These studies seek to extend the basic work of GIBBS (1906) on the equilibrium of fluid phases to the more general case of equilibrium of two coherent solid phases. While it has become a widely accepted view that 'it is not possible usefully to associate a chemical potential or Gibbs free energy with a nonhydrostatically stressed solid' (KAMB, 1961), there exists in fact in the theory of diffusionless coherent phase transformations an appropriately generalized tensorial chemical potential, as was shown recently by GRINFEL'D (1982) and independently and within a wider theoretical framework by the authors (LEHNER and HEIDUG, 1983). In reporting on the latter work in the following we shall derive a condition for unconstrained chemical equilibrium between two stressed solid phases in coherent contact, which is readily recognized as the appropriate generalization of Gibbs's classical result for fluid phases. This will be accomplished through a clear definition of coherence—as continuity of motion

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across the phase boundary—and subsequent use of Hadamard's well-known conditions of geometric and kinematic compatibility (see, e.g., TRUESDELL and TOUPIN, 1960) for the deformation gradients and particle velocities on either side of a phase boundary, conceived here as singular surface of order 1. As will be seen presently, the equilibrium condition so obtained is formally identical with an earlier result which, albeit in a mechanical disguise, already appears in the work of ESHELBY (1970), where its thermodynamic significance becomes apparent upon replacing of an isothermal elastic strain energy by a Helmholtz free energy. The same is true for a result obtained by JAMES (1981) in his work on mechanical twinning.

Although ESHELBY (1970, 1975) had appropriately viewed the jump discontinuity in the normal component of an energy-momentum tensor across a phase boundary as a generalized (thermodynamic) force, his result went unnoticed in collateral work on the thermodynamics of solids, except for a remark made by RICE (1975), who pointed out the use of this force in the development of an internal variable theory of inelastic bulk deformation of materials which undergo diffusionless phase transformations on a microscale.

The concept of a generalized force places the study of first-order phase transformations in the wider framework of nonequilibrium thermodynamics, and it is this point of view that is taken here. Accordingly, we shall first derive an expression for the interfacial entropy production in the form of a 'dissipation jump condition' for the phase boundary. The condition for unconstrained phase equilibrium then follows from the requirement that the thermodynamic force which drives the transformation must vanish simultaneously with its conjugate flux. Furthermore, this dissipation jump condition will allow us to identify the correct linear phenomenological relations for modelling near-equilibrium phase-transformation kinetics under conditions of non-hydrostatic stress.

2. Coherent phase boundaries

We consider a solid with particles identified by their positions \( \mathbf{X} \) in some reference configuration and undergoing a motion \( \mathbf{x}(\mathbf{X}, t) \), where \( \mathbf{x} \) denotes the position of the particle \( \mathbf{X} \) at time \( t \). We imagine this solid to undergo a first-order phase transformation, in the course of which a sharp phase boundary advances through it. We focus on a portion of the solid currently subdivided by the phase boundary into transformed and untransformed material, as shown in Figure 1. This portion occupies the regions \( R \) and \( R_t \), respectively, in reference and current configuration where the phase boundary is represented by the surfaces \( S(t) \) and \( s(t) \), respectively.

The surface \( s(t) \) is assumed smooth enough to possess everywhere a unique tangent plane with unit normal \( \mathbf{n} \) pointing into \( R_t^{+} \). It is assumed to be a singular surface of order 1 with respect to the motion of all mass points in \( R_o \), meaning that the function \( \mathbf{x}(\mathbf{X}, t) \) and its inverse are continuous across \( s(t) \), whereas their derivatives with respect