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Theory of strain phase separation and strain spinodal: Applications to ferroelastic and ferroelectric systems

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ABSTRACT

In the well-known phase decomposition process, a phase with a homogeneous composition separates into two phases with different local compositions that can be geometrically determined by the common tangent construction on the molar free energy versus composition curves. Here we consider an analogous phase destrain process in which a phase with a homogeneous strain separates into two phases with different local strains that can be geometrically determined by the common tangent construction on the volume free energy density versus strain curves. There is also a complete analogy between compositional and strain spinodals. Within the phase destrain model, we provide a general thermodynamic formulation for the phase rule, lever rule, equilibrium conditions of chemical potential, and coherent/incoherent strain spinodals. Using the cubic to tetragonal ferroelastic/ferroelectric transition as an example, we study the possible strain phase separation and spinodal phenomena, and calculate the strain-strain and strain-temperature phase diagrams for the first-order proper, first-order improper, and second-order improper ferroelastic transitions. The proposed phase destrain theory complements the existing compositional phase separation theory and can serve as guidance for the analysis and design of multi-domain/multi-phase structures during any phase transitions associated with structural changes.

1. Introduction

Phase separation from an initially homogeneous state to “domains” with different compositions or structures is the manifestation of a common mode of materials instability [1–3]. A prominent example is the phase decomposition process, which results in the coexistence of multiple phases with different chemical compositions [4]. For a phase decomposition process, the equilibrium free energy and local compositions of the mixed phases can be determined by the common tangent construction on the molar Gibbs free energy G_m (or the chemical potential of the system) versus composition curves as shown in Fig. 1(a). The Gibbs free energy is used for the decomposition analysis since its natural variables are temperature and pressure, which can be easily controlled in practice. A special case is the spinodal decomposition within the compositional instability regions, as shown in Fig. 1(c). The underlying physics of the common tangent construction is that the chemical potential of each species is uniform at equilibrium, i.e., $\mu_A^\alpha = \mu_A^\beta$, and $\mu_B^\alpha = \mu_B^\beta$ [1,5].

Phase separation may take place with respect to other molar extensive thermodynamic variables, and its thermodynamic equilibrium and local values of the molar variables of interest in the phase/domain mixture can also be geometrically determined by the common tangent construction. This can be easily understood from the differential form of the fundamental equation of thermodynamics,

$$dU_m = TdS_m - pdV_m + \sum_{i=1}^{n} \mu_i dx_i + V_m \sum_{i,j=1}^{3} \sigma_{ij} d\varepsilon_{ij}, \tag{1}$$

where U_m, T, S_m, p, and V_m are molar internal energy, temperature, molar entropy, pressure, and molar volume, respectively, μ_i and x_i are chemical potential and mole fraction of species i, n is the number of chemical components, and ε_{ij} and σ_{ij} are strain and stress components.

The thermodynamic states determined from the common tangent construction on the free energy versus a molar extensive variable curves possess the same values for the corresponding intensive variable, i.e., the intensive variable is uniform throughout the system at equilibrium. For example, the common tangent construction can be applied to the free energy versus molar volume

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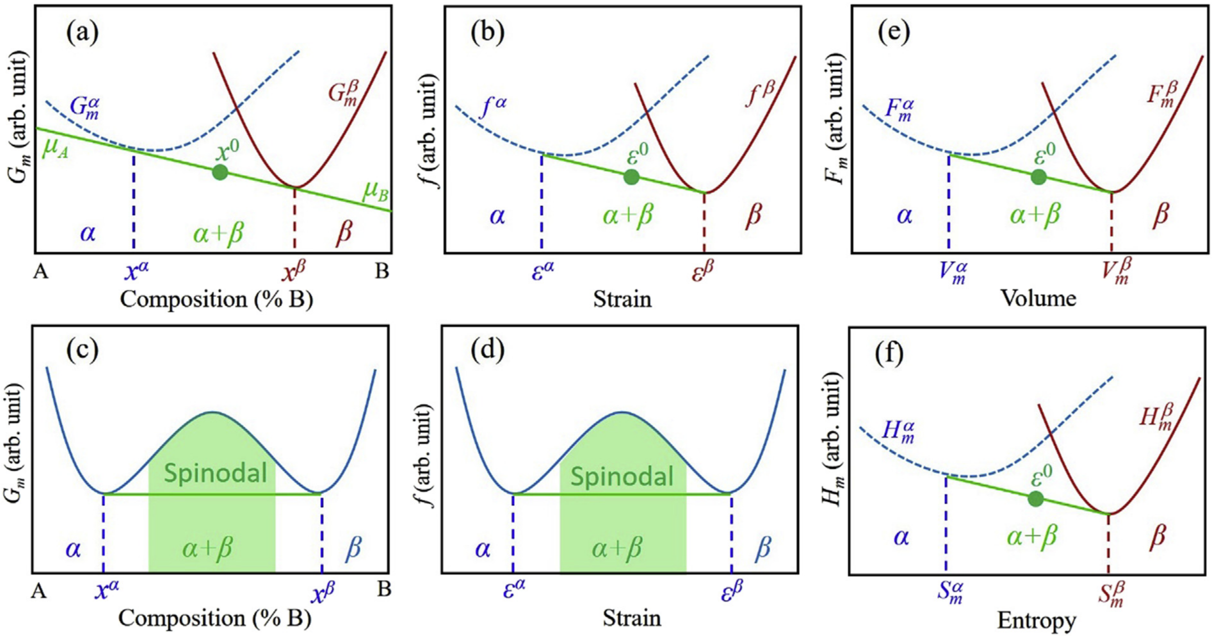

Fig. 1. Schematics of different phase separation processes. Common tangent constructions for (a) phase decomposition, (b) phase/domain destrain, (c) spinodal decomposition, (d) strain spinodal, (e) volume phase separation, and (f) entropy phase separation. In (a)–(f), G_m, f, F_m, H_m, V_m, and S_m denote molar Gibbs free energy, volume Helmholtz free energy density, molar Helmholtz free energy, molar enthalpy, molar volume, and molar entropy, respectively. In (c) and (d), the shaded regions represent spinodal decomposition, and strain spinodal, respectively.

or molar entropy curves, as shown in Fig. 1(e) and (f), where the states lying on the common tangents have the same pressure or temperature, respectively. Similarly, as it has been reported in our short communication [6], the coexistence of domains with different local strains can be interpreted using a new concept, "phase destrain", analogous to the phase decomposition process. As shown in Fig. 1(b) and (d), the equilibrium free energy and local strains of different domains can be determined by the common tangent construction on the Helmholtz free energy density versus strain curves. The Helmholtz free energy is used for the destrain process since strain components are its natural variables.

In this work, we present a general thermodynamic formulation for the destrain process, i.e., phase separation of a homogeneous strain phase into a mixture of several structural domain/phase variants with different strains. The multi-domain structure resulted from a strain phase separation is a key factor for determining the mechanical and functional properties of a crystal, e.g., the stress-strain hysteresis loops, shape-memory effect of martensitic crystals, and the dielectric and piezoelectric responses of a ferroelectric crystal. Furthermore, such multi-phase structures can be strain-engineered to produce dramatically enhanced responses under external stimuli due to the easy transition among the two or more different phases [7–9]. Therefore, the proposed domain/phase destrain theory is not only important for predicting the equilibrium multi-domain states but also for the fundamental understanding of the mechanical and functional properties of materials, and thus it will be a useful theory for providing guidance to design useful devices with superior functionality through strain engineering [10,11].

One of the best examples for the destrain process is the coexistence of structural domain variants during a ferroelastic phase transition under a fixed external strain, e.g., epitaxial strain in a thin film constrained by a substrate. A ferroelastic transition refers to a solid state phase transition characterized by the spontaneous lattice deformation, which produces a point-group symmetry reduction of the parent phase and leads to the appearance of different deformation variants, i.e., different domains [12,13]. The number of possible domain variants is determined by the group-subgroup symmetry relationships between the high symmetry phase and the low symmetry phase. For example, in a cubic to tetragonal ferroelastic transition, the number of possible deformation strain variants is three with the tetragonal axis along [100], [010], or [001] directions of the cubic phase. Each lattice deformation variant is described by a transformation strain, i.e., an eigen-strain under stress-free boundary conditions or simply a stress-free strain [14]. Therefore, within the destrain model, the transformation process of the high symmetry phase into the mixture of domain orientation variants of the lower symmetry phase is regarded as a strain phase separation of an initially homogeneous phase into several phases with different transformation strains. The volume fractions of each strain variant is determined by the overall strain, in analogy to the lever rule in the chemical decomposition process with the volume fractions of each phase determined by the overall composition.

The thermodynamic discussions presented in this article are applicable to any ferroelastic systems regardless whether the ferroelastic transition is a proper ferroelastic transition with strain as the primary order parameter or improper ferroelastic transitions in which strain is a secondary order parameter. Examples of proper ferroelastic transitions include the cubic to tetragonal transitions in steels [12], Ni–Ti-based shape-memory alloys [15], and Heusler-type shape-memory alloys [16,17]. Usually a proper ferroelastic transition is a first-order transition with discontinuous change of strain at the transition temperature. On the other hand, in an improper ferroelastic phase transition, strain is a secondary effect, and the leading transition mode can be the relative displacement of atoms described by "soft mode" or other electronic transitions. In an improper ferroelastic transition, strain is a quadratic function of the primary order parameter [18,19]. Depending on the behavior of the primary order parameter, an improper ferroelastic transition can be either first-order or second-order. In a first-order transition, the primary order parameter and the associated strain are discontinuous at the transition temperature, whereas in a second-order