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Phase field approach for stress- and temperature-induced phase transformations that satisfies lattice instability conditions. Part I. General theory

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Abstract

Recently, results of molecular dynamics (MD) simulations were obtained for the crystal lattice instability conditions for the phase transformations (PTs) between semiconducting Si I and metallic Si II under action of all six components of the stress tensor (Levitas et al. (2017a,b)). These conditions are linear in terms of stresses normal to the cubic faces of Si I and are independent of the shear stresses. In the current paper, we (a) formulated the requirements for the thermodynamic potential and transformation deformation gradient tensors and (b) developed a phase field approach (PFA) for the stress-induced martensitic PTs for large strains while allowing for interfacial stresses, which are consistent with the obtained instability conditions. The general system of equations for coupled PFA and non-linear elasticity is presented. Crystal lattice instability criteria are derived within a PFA, and it is proven that they are independent of the prescribed stress measure. In order to reproduce the lattice instability conditions obtained with MD: (a) one has to use the fifth degree polynomial interpolation functions of the order parameter for all material parameters; (b) each component of the transformation strain tensor should have a different interpolation

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functions; and (c) the interpolation functions for tensors of the elastic moduli of all ranks should have zero second derivatives for the parent and product phases, so that terms with elastic moduli, which are nonlinear in stresses, do not contribute to the lattice instability conditions. Specific interpolation and double-well functions have been derived for all parts of the Helmholtz free energy and for two models for the transformation deformation gradient. For these models, explicit expressions for the Ginzburg-Landau equations and lattice instability conditions are derived. Material parameters have been calibrated using results of MD simulations. In Part II of this paper, the developed model is further refined and studied, and applied for the finite element simulations of the nanostructure evolution in Si under triaxial loading.

Keywords:

phase-field approach, martensitic phase transformation, lattice instability condition, interpolation functions, large strains

1. Introduction

The PFA is broadly used for modeling martensitic PTs (Artemev et al. (2001); Chen (2002); Jin et al. (2001a); Levitas and Preston (2002a,b); Levitas et al. (2003); Mamivand et al. (2014); Mamivand and Zaeem (2013); Paranjape et al. (2016); Rogovoy and Stolbova (2016); Wang and Khachaturyan (2006); Zhu et al. (2017)) and reconstructive PTs (Denoual et al. (2010); Salje (1990)). Here, we will consider the PT between the parent phase P_0 and the product phase P_1 , without including multiple symmetry-related martensitic variants for brevity. This PT is parameterized by the order parameter η , with $\eta = 0$ for the phase P_0 and $\eta = 1$ for the phase P_1 . The Helmholtz free energy consists of both the local part and gradient energy $0.5\beta|\nabla\eta|^2$, the latter penalizes the interface energy. Some theories (Artemev et al. (2001); Chen (2002); Jin et al. (2001a); Wang and Khachaturyan (2006)) did not specify the physical meaning of the order parameter, but others utilized some components of the

strain tensor as the order parameters (Barsch and Krumhansl (1984); Falk (1983); Finel et al. (2010); Jacobs (1992); Vedantam and Abeyaratne (2005)).

The key points in formulating the local thermodynamic potential is to interpolate all material properties along the transformation paths and to introduce proper energetic barriers between phases. The only requirements imposed in Artemev et al. (2001); Barsch and Krumhansl (1984); Chen (2002); Falk (1983); Finel et al. (2010); Jacobs (1992); Jin et al. (2001a); Vedantam and Abeyaratne (2005); Wang and Khachaturyan (2006) for the local energy are that it has as many local minima as there are phases (including martensitic variants) that one considers and that the energy is invariant with respect to an exchange of any symmetry-related martensitic variants, which is sufficient for qualitatively reproducing a complex multivariant martensitic structure. As a consequence, the order parameter for the product phase P_1 was not fixed to 1 but depended on stresses and temperature. This did not allow for precisely reproducing the known material properties of the product phase. In Levitas and Preston (2002a,b); Levitas et al. (2003) additional important requirements have been formulated, which will be discussed below and which results in constraint Eqs.(12) and (16) for an interpolation function $\varphi_m(\eta)$ for any material property M . Also, the PT criteria for direct and reverse PTs should follow from the crystal lattice instability criteria. The PFAs that satisfy these requirements have been developed within the fourth degree potential (2 – 3 – 4) in terms of the order parameter and the six degree potential (2 – 4 – 6) in terms of the even degrees of η . These theories reproduce desired stress-strain curves. The order parameter in Levitas and Preston (2002a,b); Levitas et al. (2003) was related to the transformation strain tensor rather than to the total strain. In fact, we did not find a way to impose these constraints for the theories based on the total strain-related order parameters, that is why they will not be considered any further. These requirements are important to ensure that the thermodynamically equilibrium material properties of both parent and product phases are reproduced in the PFA, which was not the case in the previous theories.

As it is shown in Levitas and Preston (2002a), the transformation strain and stress hysteresis in Artemev et al. (2001); Barsch and Krumhansl (1984); Chen (2002); Falk (1983); Finel et al. (2010); Jacobs (1992); Jin et al. (2001a); Vedantam and Abeyaratne (2005); Wang and Khachaturyan (2006) strongly depend on temperature, and stress-strain curves do not reproduce the main features observed in experiments for shape memory alloys, steels, and some ceramics.

The PFA developed in Levitas and Preston (2002a,b); Levitas et al. (2003) was applied for modeling microstructure evolution during multivariant martensitic PTs (Cho et al. (2012); Idesman et al. (2008); Levitas and Lee (2007); Levitas et al. (2010)). It was also generalized for large strain formulation in Levitas (2013a); Levitas et al. (2009) with corresponding finite element simulations in Levin et al. (2013). This approach was based on the interpolation of the transformation deformation gradient between parent and product phases.

It was found in Tuma and Stupkiewicz (2016); Tuma et al. (2016) that such an interpolation does not allow for properly separating the volumetric part of the transformation strain and change in shape. In particular, for twinning it produces volume-conserving shear after complete transformation only, while there is a volume change during the transformation. Interpolation of the logarithmic transformation strain which keeps the volume conserved was suggested in Tuma and Stupkiewicz (2016); Tuma et al. (2016). This was done within the theory which uses volume fraction of phases as order parameters, which is suitable for the microscale models (as in Idesman et al. (2005); Levitas et al. (2004)) but not for the nanoscale ones. However, it was shown in Basak and Levitas (2017) that interpolation for logarithmic transformation strain produces artificial elastic interfacial stress for a variant-variant interface which are more than two times larger than for the interpolation used in Levitas (2013a); Levitas et al. (2009).

Interfacial stresses for martensitic PTs were introduced in Levitas (2013b,c, 2014a); Levitas and Javanbakht (2010) for small strain formulation. These theories were generalized for

large strains in Levitas (2014b) for isotropic interface energy and stresses and in Levitas and Warren (2016) for an anisotropic case. However, the lattice instability conditions in Levitas (2013a) were not yet extended for the model with interfacial stresses, which will be done in the current study.

In the previous theories the constraint on the interpolation functions were limited to the values of the functions and their first derivatives at $\eta = 0$ and 1, see Eqs.(12) and (16). The lattice instability conditions operate with the second derivatives of the interpolation functions (Levitas (2013a); Levitas and Preston (2002a,b); Levitas et al. (2003)); however, since they were not known from experiment or atomistic simulations, no limitations were imposed. At the same time, lattice instability conditions are crucial for understanding barrierless nucleation during martensitic and reconstructive PTs for relatively low temperatures, when thermal fluctuations play a minor part (Olson and Cohen (1972, 1986); Olson and Roytburd (1995)). They are especially important for high pressure PTs for which transformation pressure is much higher than the phase equilibrium pressure. For example, the phase equilibrium pressure for the PT from hexagonal to superhard cubic BN at room temperature is even negative (i.e., cubic BN is stable at atmospheric pressure), see Solozhenko (1995); however, highly disordered hexagonal BN does not transform up to at least 52 GPa, i.e., lattice instability pressure is even higher (Ji et al. (2012)).

Recently, lattice instability conditions for the PTs between semiconducting Si I and metallic Si II under action of all six components of the stress tensor were found with the help of MD simulations (Levitas et al. (2017a,b)). These conditions are linear in terms of stresses normal to the cubic faces of Si I, σ_i , and are independent of the shear stresses. Thus, the instability conditions can be presented in a 3D stress space σ_i as two planes (Figs. 4 and 5), one for direct and another for reverse PTs. It is important that these planes are not parallel and consequently not consistent with the instability conditions within 2 – 3 – 4 and 2 – 4 – 6 thermodynamic potentials. In addition, after the intersection of these planes they

coincide for part of the stress space (Fig. 5). Thus, new conditions have to be formulated for the interpolation functions in order to make phase field equations consistent with the lattice instability conditions obtained with MD simulations and new PFA should be developed that satisfies these conditions.

The paper is organized as follows. General PFA for martensitic PT described by a single order parameter is presented in Section 2 for large strains while allowing for interfacial stresses. Further consideration is limited to the homogeneous transformation processes. A thermodynamic equilibrium condition for the order parameter and its consequence for the constraints on the interpolation functions are considered in Section 3. In Section 4 the criterion for the crystal lattice instability of the thermodynamically equilibrium homogeneous states under homogeneous perturbations is derived for the theory, which includes interfacial stresses. In particular, this was done for the prescribed first Piola-Kirchoff stress in Section 4.1; generalized for an arbitrary prescribed stress in Section 4.2, and conditions for interpolation functions were summarized in Section 4.3. Examples of the fifth-degree interpolation functions and double-well barrier functions that satisfy the formulated conditions were presented in Sections 5 and 6, respectively. In Section 7 specific expressions for the thermal part of the free energy and corresponding lattice instability conditions for a stress-free case were derived. Thermal energy is divided into two parts: the first contributes to the interfacial stresses and the other does not. In Section 8 expressions for the transformation deformation gradient are presented. Both kinematic models, based on interpolation of the transformation strain and logarithmic transformation strain, are presented and analyzed. For the second model the desired results are obtained when interpolation is performed separately for spherical and deviatoric parts of the logarithmic transformation strain. An expression for high order elastic energy and the lattice instability criteria for the chosen interpolation functions are presented. Specification for Si I \leftrightarrow Si II phase transformations is performed in Section 9 utilizing the results of the MD simulations. In order to reproduce the lattice instability

conditions obtained with MD:

- (a) each component of the transformation strain tensor should have a different interpolation function and
- (b) interpolation functions for tensors of the elastic moduli of all ranks should have zero second derivatives at $\eta = 0$ and 1 so that the nonlinear-in-stresses elastic energy does not spoil linear-in-stresses lattice instability conditions.

Explicit expressions for the thermodynamic driving forces and lattice instability conditions are derived for both kinematic models. Parameter identification for PTs between diamond cubic phase Si I and β -tin phase Si II under action of three stresses normal to the cubic faces was performed for both kinematic models, with emphasis on satisfying lattice instability conditions. Concluding remarks are presented in Section 10. In Part II of this paper (Levitas (2018)), the developed model will be further refined and studied, and applied for the finite element simulations of the nanostructure evolution during Si I \leftrightarrow Si II PTs under various triaxial loadings. Various phenomena and stress evolution, especially interfacial stresses will be analyzed.

We designate vectors and tensors with boldface symbols and designate contractions of tensors $\mathbf{A} = \{A_{ij}\}$ and $\mathbf{B} = \{B_{ji}\}$ over one and two indices as $\mathbf{A} \cdot \mathbf{B} = \{A_{ij} B_{jk}\}$ and $\mathbf{A} : \mathbf{B} = A_{ij} B_{ji}$. The transpose of \mathbf{A} is \mathbf{A}^T , and \mathbf{I} is the unit tensor; symbol \forall means "for all", $:=$ means equal by definition; ∇ and ∇_0 are the gradient operators with respect to the deformed and undeformed states.

2. General Theory

Kinematics. The motion of elastic material with PTs will be described by a continuous vector function $\mathbf{r} = \mathbf{r}(\mathbf{r}_0, t)$, where \mathbf{r}_0 and \mathbf{r} are the positions of points in the reference (undeformed) Ω_0 and the actual (deformed) Ω configurations, respectively; t is the time.

The deformation gradient $\mathbf{F} = \frac{\partial \mathbf{r}}{\partial \mathbf{r}_0} = \nabla_0 \mathbf{r}$ can be multiplicatively decomposed

$$\mathbf{F} = \mathbf{F}_e \cdot \mathbf{U}_t, \quad (1)$$

into elastic and transformational parts (Levitas (1998)). Without loss of generality, thermal strain is included in $\mathbf{U}_t(\eta)$, $\mathbf{U}_t(\eta)$ is considered to be symmetric (rotation-free) tensor, and all rotations are included in \mathbf{F}_e . After a local release of stresses, elastic deformation disappears (i.e., $\mathbf{F}_e = \mathbf{I}$) and an unloaded configuration, characterized by \mathbf{U}_t , is designated as Ω_t . It is assumed that no reverse PT occurs during such an unloading; otherwise, these procedures should be considered as the thought experiment under fixed phase state. The Jacobian determinants, which describe ratios of volumes V and mass densities ρ in the corresponding configurations, are

$$J := \frac{dV}{dV_0} = \frac{\rho_0}{\rho} = \det \mathbf{F}; \quad J_t := \frac{dV_t}{dV_0} = \frac{\rho_0}{\rho_t} = \det \mathbf{U}_t; \quad J_e := \frac{dV_e}{dV_\theta} = \frac{\rho_\theta}{\rho_e} = \det \mathbf{F}_e \Rightarrow J = J_t J_e. \quad (2)$$

Dissipation rate, equations for stresses, and Ginzburg-Landau equation. Using the first and second laws of thermodynamics, and accepting the Helmholtz free energy per unit mass in the form $\psi = \bar{\psi}(\mathbf{F}, \eta, \theta, \nabla_0 \eta)$, the dissipation rate per unit mass D due to phase transformation can be derived as follows (Levitas (2014b)):

$$D = X \dot{\eta} \geq 0; \quad \rho_0 X := -\rho_0 \frac{\partial \bar{\psi}}{\partial \eta} + \nabla_0 \cdot \left(\rho_0 \frac{\partial \bar{\psi}}{\partial \nabla_0 \eta} \right), \quad (3)$$

where X is the thermodynamic force per unit mass for change in η and θ is the temperature. The same thermodynamic procedure leads to the expression for the first Piola–Kirchhoff stress \mathbf{P} and the true Cauchy stress $\boldsymbol{\sigma}$, as well as for the entropy s :

$$\mathbf{P} = \rho_0 \frac{\partial \bar{\psi}}{\partial \mathbf{F}}; \quad \boldsymbol{\sigma} := J^{-1} \mathbf{P} \cdot \mathbf{F}^t = \rho \frac{\partial \bar{\psi}}{\partial \mathbf{F}} \cdot \mathbf{F}^t; \quad s = -\frac{\partial \bar{\psi}}{\partial \theta}, \quad (4)$$

where viscous stresses are neglected for compactness. The linear relationship between generalized thermodynamic force X and rate $\dot{\eta}$ results in the generalized Ginzburg-Landau

equation

$$\dot{\eta} = LX = L \left(-\frac{\partial \bar{\psi}}{\partial \eta} + \frac{1}{\rho_0} \nabla_0 \cdot \left(\rho_0 \frac{\partial \bar{\psi}}{\partial \nabla_0 \eta} \right) \right), \quad (5)$$

where $L > 0$ is the kinetic coefficient.

Specification of the Helmholtz energy. To introduce interface tension, we accept the Helmholtz free energy per unit mass in the following form (Levitas (2014b)):

$$\begin{aligned} \bar{\psi}(\mathbf{F}, \eta, \theta, \nabla_0 \eta) &= \psi^l(\mathbf{F}, \eta, \theta) + J \psi^\nabla(\mathbf{F} \cdot \nabla_0 \eta) = \\ &= \frac{J_t}{\rho_0} \psi^e(\mathbf{F}_e, \eta, \theta) + J \check{\psi}^\theta + \tilde{\psi}^\theta + J \psi^\nabla(\nabla \eta); \quad \psi^\nabla = \frac{\beta}{2\rho_0} |\nabla \eta|^2. \end{aligned} \quad (6)$$

Here ψ^l is the local and ψ^∇ is the gradient energies; ψ^e is the elastic energy, $\beta > 0$ is the gradient energy coefficient; $\tilde{\psi}^\theta$ is the part of the thermal energy, which is proportional to the thermal driving force for $P_0 \rightarrow P_1$ PT $\Delta\psi^\theta = \psi_1^\theta - \psi_0^\theta$, and $\check{\psi}^\theta$ is the double-well energy, which may also depend on $\Delta\psi^\theta$. As it was demonstrated in Levitas (2014b) the consideration of the gradient $\nabla \eta = \nabla_0 \eta \cdot \mathbf{F}^{-1}$ in the deformed configuration as an argument of ψ^∇ and multiplication of $\check{\psi}^\theta$ and ψ^∇ by the Jacobian determinant J results (with the proper choice of $\check{\psi}^\theta$) in the desired expression for interface stresses. Note that Jacobians and gradient with respect to deformed configurations in Eq.(6) should be kept even in small strain formulation (when they are traditionally neglected), otherwise, interface stresses will disappear, see Levitas (2013b). The reason for the multiplier $\frac{J_t}{\rho_0}$ in front of the elastic energy is described in Levitas (2014b). Note that since $\mathbf{F}_e = \mathbf{F} \cdot \mathbf{U}_t^{-1}(\eta)$, dependence of ψ^e on \mathbf{F}_e and η does not contradict the structure of the free energy $\bar{\psi}(\mathbf{F}, \eta, \theta, \nabla_0 \eta)$. Due to the principle of material frame-indifference, $\psi^e = \psi^e(\mathbf{E}_e, \eta, \theta)$, where $\mathbf{E}_e = 0.5(\mathbf{F}_e^T \cdot \mathbf{F}_e - \mathbf{I})$ is the Lagrangian elastic strain, and we did not change designation of the function for elastic energy for brevity.

Explicit equations for stresses. For such a structure of the free energy, one obtains (Levitas

(2014b)) the following relationships for the first Piola–Kirchhoff stress

$$\begin{aligned} \mathbf{P} &= \mathbf{P}_e + \mathbf{P}_{st}; & \mathbf{P}_e &= J_t \frac{\partial \psi^e}{\partial \mathbf{F}_e} \cdot \mathbf{U}_t^{-1}; \\ \mathbf{P}_{st} &= \rho_0 J(\check{\psi}^\theta + \psi^\nabla) \mathbf{F}^{t-1} - \rho_0 J \nabla \eta \otimes \frac{\partial \psi^\nabla}{\partial \nabla \eta} \cdot \mathbf{F}^{t-1} = \\ &J(\rho_0 \check{\psi}^\theta + \frac{\beta}{2} |\nabla \eta|^2) \mathbf{F}^{t-1} - J \beta \nabla \eta \otimes \nabla \eta \cdot \mathbf{F}^{t-1}, \end{aligned} \quad (7)$$

and for the Cauchy stress

$$\begin{aligned} \boldsymbol{\sigma} &= \boldsymbol{\sigma}_e + \boldsymbol{\sigma}_{st}; & \boldsymbol{\sigma}_e &= J_e^{-1} \mathbf{F}_e \cdot \frac{\partial \psi^e}{\partial \mathbf{E}_e} \cdot \mathbf{F}_e^t = J_e^{-1} \mathbf{V}_e \cdot \frac{\partial \psi^e}{\partial \mathbf{B}_e} \cdot \mathbf{V}_e; \\ \boldsymbol{\sigma}_{st} &= \rho_0(\check{\psi}^\theta + \psi^\nabla) \mathbf{I} - \rho_0 \nabla \eta \otimes \frac{\partial \psi^\nabla}{\partial \nabla \eta} = (\rho_0 \check{\psi}^\theta + \frac{\beta}{2} |\nabla \eta|^2) \mathbf{I} - \beta \nabla \eta \otimes \nabla \eta. \end{aligned} \quad (8)$$

Here, elastic stresses (designated with the subscript e) are defined in terms of elastic energy of the bulk phases; structural stresses (designated with the subscript st) are zero in bulk and localize at the interface between phases. It is proven in Levitas (2014b) that for the propagating interface $\boldsymbol{\sigma}_{st}$ reduces to biaxial stress with a magnitude equal to the nonequilibrium interface energy.

Explicit form of the Ginzburg-Landau equation. Similarly, substituting free energy Eq.(6) in the Ginzburg-Landau equation (5), after the transformation presented in Levitas (2014b), results in the following expression in the reference configuration

$$\begin{aligned} \dot{\eta} = LX &= \frac{L}{\rho_0} \left(\mathbf{P}_e^t \cdot \mathbf{F}_e : \frac{d\mathbf{U}_t(\eta)}{d\eta} - J_t \frac{\partial \psi^e}{\partial \eta} \Big|_{\mathbf{F}_e} - J_t \psi^e \mathbf{U}_t^{-1} : \frac{d\mathbf{U}_t}{d\eta} \right. \\ &\left. - J \rho_0 \frac{\partial \check{\psi}^\theta}{\partial \eta} - \rho_0 \frac{\partial \tilde{\psi}^\theta}{\partial \eta} + J \beta (\mathbf{F}^{-1} \cdot \mathbf{F}^{t-1}) : \nabla_0 \nabla_0 \eta \right) \end{aligned} \quad (9)$$

and in the current configuration

$$\begin{aligned} \frac{D\eta(\mathbf{r}, t)}{Dt} &= \frac{\partial \eta(\mathbf{r}, t)}{\partial t} + \mathbf{v} \cdot \nabla \eta = LX = \frac{L}{\rho} \left(\mathbf{F}_e^t \cdot \boldsymbol{\sigma}_e : \mathbf{F}_e^{t-1} \cdot \mathbf{U}_t^{-1} : \frac{d\mathbf{U}_t(\eta)}{d\eta} \right. \\ &\left. - \frac{1}{J_e} \frac{\partial \psi^e}{\partial \eta} \Big|_{\mathbf{E}_e} - \frac{\psi^e}{J_e} \mathbf{U}_t^{-1} : \frac{d\mathbf{U}_t}{d\eta} - \rho_0 \frac{\partial \check{\psi}^\theta}{\partial \eta} - \frac{\rho_0}{J} \frac{\partial \tilde{\psi}^\theta}{\partial \eta} + \beta \nabla^2 \eta \right), \end{aligned} \quad (10)$$

where \mathbf{v} is the particle velocity. Note that the structural stresses do not directly contribute to the driving force X . However, the structural stresses change elastic stresses through the solution of the mechanical problem and contribute to X indirectly.

3. Thermodynamic equilibrium conditions for homogeneous phases

Determination of η -dependence of \mathbf{U}_t and all material properties entering the free energy ψ is one of the main problems in formulating the phase field theories. Here we will formulate the main conditions, which should be satisfied while formulating specific theories.

Independent of the physical interpretation of the order parameter, it can be modified so that $\eta = 0$ corresponds to the phase P_0 and $\eta = 1$ corresponds to the phase P_1 . Both thermodynamically equilibrium values of η , 0 and 1, will be for brevity designated by a symbol $\hat{\eta}$. It is natural to present any material property M (energy, entropy, elastic moduli and thermal expansion) in the form

$$M(\eta, \theta) = M_0(\theta) + (M_1(\theta) - M_0(\theta))\varphi_m(\eta). \quad (11)$$

Here M_0 and M_1 are values of the property M at $\eta = 0$ and $\eta = 1$, respectively, and $\varphi_m(\eta)$ is the interpolation function that meets evident constraints

$$\varphi_m(0) = 0, \quad \varphi_m(1) = 1. \quad (12)$$

Since $\eta = 0$ corresponds to the homogeneous bulk phase P_0 and $\eta = 1$ corresponds to the homogenous bulk phase P_1 , the order parameter should not evolve further after reaching equilibrium bulk phases. According to the Ginzburg-Landau Eq.(9) for homogeneous states, this is possible when for bulk phases the thermodynamic equilibrium condition is identically satisfied. Thus, values $\eta = 0$ and $\eta = 1$ should satisfy the thermodynamic equilibrium

conditions

$$\begin{aligned} \rho_0 X = \mathbf{P}^t \cdot \mathbf{F}_e : \frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} - J_t \frac{\partial \psi^e(\mathbf{E}_e, \theta, \hat{\eta})}{\partial \eta} \Big|_{\mathbf{F}_e} - J_t \psi^e(\mathbf{E}_e, \theta, \hat{\eta}) \mathbf{U}_t^{-1} : \frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} \\ - J \rho_0 \frac{\partial \check{\psi}^\theta(\theta, \hat{\eta})}{\partial \eta} - \rho_0 \frac{\partial \tilde{\psi}^\theta(\theta, \hat{\eta})}{\partial \eta} = 0 \end{aligned} \quad (13)$$

for any stress \mathbf{P} , temperature θ , and corresponding elastic deformation gradient \mathbf{F}_e . Note that for homogeneous states structural stresses disappear and elastic stresses remain only. That is why we will omit subscript e for stresses when possible.

If the above condition is not met, the thermodynamic equilibrium values of the order parameters obtained from condition $X = 0$ will depend on stresses and temperature. Inserting these functions in Eq.(11) will result in an artificial stress- and temperature-dependence of the property M , which will not coincide with the known properties M_0 and M_1 of bulk phases. Eq.(13) can be presented in a more concise form:

$$\rho_0 X = \mathbf{P}^T \cdot \mathbf{F}_e : \frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} - \rho_0 \frac{\partial \psi^l(\mathbf{E}_e, \theta, \hat{\eta})}{\partial \eta} = 0 \quad (14)$$

Due to the independence of \mathbf{U}_t and ψ^l , Eq.(14) splits in two sets of equations:

$$\frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} = 0; \quad \frac{\partial \psi^l(\mathbf{E}_e, \theta, \hat{\eta})}{\partial \eta} = 0. \quad (15)$$

It also follows from Eq.(15) that for transformation deformation gradient and any material property which participates in ψ^l , one has

$$\frac{d\varphi_m(0)}{d\eta} = \frac{d\varphi_m(1)}{d\eta} = 0. \quad (16)$$

Note that one of the important assumptions is that η is not subjected to any constraint, like e.g., $\eta \in [0, 1]$, which is the case for volume fraction of a phase, see Folch and Plapp (2003, 2005); Idesman et al. (2005); Steinbach (2009); Tuma and Stupkiewicz (2016); Tuma et al. (2016). In those theories extrema at $\eta = 0$ and $\eta = 1$ may be because of constraint rather than zero derivative. This case is explicitly excluded in the current study.

4. Criterion for the instability of the thermodynamically equilibrium homogeneous states under homogenous perturbations

PT criteria in PFA are usually derived as conditions for instability of the homogeneous equilibrium state of crystal lattice under spontaneous variation of the order parameters, see the most general finite-strain treatment in Levitas (2013a); Levitas et al. (2017b). In contrast, the traditional instability approach originated in Born (1939, 1940) and generalized for the finite strain in Hill and Milstein (1977); Milstein et al. (1995); Wang et al. (1993a) is based on the elastic lattice instability. Extra degrees of freedom are included in stability analysis for multilattices, namely, relative shift vectors (see Dove (1993); Elliott et al. (2011)). In addition, phonon stability criteria (see Dove (1993); Elliott et al. (2011)) were applied. Some advantages of our approach based on the order parameters and comparison of different approaches are presented in Levitas (2017); Levitas et al. (2017b). We will not repeat it here and will present our approach only.

4.1. Instability under prescribed first Piola-Kirchoff stress \mathbf{P}

Instability of the homogeneous equilibrium state, i.e., phase P_0 or P_1 , under homogeneous perturbations, i.e., for material point, can only be analyzed for prescribed boundary conditions for some stress measure. It does not mean that stresses $\boldsymbol{\sigma}$ or \mathbf{P} , which directly participate in boundary conditions, can be prescribed only. With the proper feedback and control of $\boldsymbol{\sigma}$ or \mathbf{P} in experiment or atomistic simulations one can prescribe any stress measure. We will start with prescribed nominal stress—i.e., the nonsymmetric first Piola-Kirchoff stress \mathbf{P} . Temperature is fixed and may be omitted when it is not important. In contrast to the study of elastic instability, when strain is subjected to a spontaneous fluctuation under prescribed stress, we consider inelastic instability characterized by spontaneous fluctuations of the internal variable or order parameter η under prescribed stress. Elastic deformation gradient \mathbf{F}_e does not have independent fluctuations and obeys the elasticity rule (7). Still,

it is allowed to vary due to change in elastic moduli during PT and spontaneous variation in η .

Definition. If under prescribed boundary conditions for any spontaneous perturbation of the order parameter $\Delta\eta$ from the thermodynamic equilibrium values $\hat{\eta}$ the dissipation rate $D \geq 0$, then this perturbation is thermodynamically admissible and the equilibrium is unstable.

Thus, if for the thermodynamically equilibrium states $\hat{\eta}$ under stress $\mathbf{P} = \text{const}$, the perturbation $\Delta\eta$ and corresponding perturbation $\Delta\mathbf{F}_e$ (that follows from the elasticity rule (7)) satisfy the thermodynamic admissibility condition

$$\rho_0 X(\mathbf{P}, \mathbf{F}_e + \Delta\mathbf{F}_e, \hat{\eta} + \Delta\eta, \theta) \dot{\eta} \geq 0, \quad (17)$$

then equilibrium of phase $\hat{\eta}$ is thermodynamically unstable. Since, $X(\mathbf{P}, \mathbf{F}_e, \hat{\eta}) = 0$, the Taylor series of X in Eq. (17) around the equilibrium values $\hat{\eta}$ leads to

$$\rho_0 \left. \frac{\partial X(\mathbf{P}, \mathbf{F}_e, \hat{\eta})}{\partial \eta} \right|_{\mathbf{P}} \dot{\eta}^2 \geq 0 \quad \rightarrow \quad \rho_0 \left. \frac{\partial X(\mathbf{P}, \mathbf{F}_e, \hat{\eta})}{\partial \eta} \right|_{\mathbf{P}} \geq 0. \quad (18)$$

Let us find an explicit expression for $\left. \frac{\partial X}{\partial \eta} \right|_{\mathbf{P}}$ by directly differentiating the expression for X from Eq. (14):

$$\begin{aligned} \rho_0 \left. \frac{\partial X}{\partial \eta} \right|_{\mathbf{P}} &= \mathbf{P}^t \cdot \frac{\partial \mathbf{F}_e}{\partial \eta} : \frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} + \mathbf{P}^t \cdot \mathbf{F}_e : \frac{d^2 \mathbf{U}_t(\hat{\eta})}{d\eta^2} - \rho_0 \left. \frac{\partial^2 \psi^l(\mathbf{E}_e, \hat{\eta})}{\partial \eta^2} \right|_{\mathbf{F}_e} \\ &\quad - \rho_0 \left. \frac{\partial^2 \psi^l(\mathbf{E}_e, \hat{\eta})}{\partial \eta \partial \mathbf{F}_e} : \frac{\partial \mathbf{F}_e^t}{\partial \eta} \right|_{\mathbf{P}}. \end{aligned} \quad (19)$$

The first term disappears because of Eq. (15), $\frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} = 0$. According to the thermoelasticity rule (7),

$$\mathbf{P} = J_t \frac{\partial \psi^e}{\partial \mathbf{F}_e} \cdot \mathbf{U}_t^{-1} \quad \rightarrow \quad \mathbf{P} = \mathbf{f}(\mathbf{F}_e, \mathbf{U}_t, M^i(\eta)), \quad (20)$$

where \mathbf{f} is some function and $M^i(\eta)$ are all material properties that participate in the elasticity rules, such as components of the elasticity tensors of different ranks and thermal expansion coefficients. Differentiating Eq. (20) at fixed \mathbf{P} one has

$$\frac{\partial \mathbf{P}}{\partial \eta} = 0 = \frac{\partial \mathbf{f}}{\partial \mathbf{F}_e^t} \cdot \frac{\partial \mathbf{F}_e(\hat{\eta})}{\partial \eta} \bigg|_{\mathbf{P}} + \frac{\partial \mathbf{f}}{\partial \mathbf{U}_t} \cdot \frac{d \mathbf{U}_t(\hat{\eta})}{d \eta} + \frac{\partial \mathbf{f}}{\partial M^i} \frac{d M^i(\hat{\eta})}{d \eta}. \quad (21)$$

The second term in Eq. (21), according to Eq. (15) $\frac{d \mathbf{U}_t(\hat{\eta})}{d \eta} = 0$. The last term in Eq. (21) also disappears, because for any property M^m , according to Eqs. (11) and (16), one has $\frac{d M^m(\hat{\eta})}{d \eta} = 0$. Then Eq. (21) represents a system of nine homogeneous linear equations with respect to $\frac{\partial \mathbf{F}_e(\hat{\eta})}{\partial \eta}$. Since in general $\det \left(\frac{\partial \mathbf{f}}{\partial \mathbf{F}_e^T} \right) \neq 0$ (excluding some special stress states), this system has the only solution

$$\frac{\partial \mathbf{F}_e(\hat{\eta})}{\partial \eta} \bigg|_{\mathbf{P}} = 0. \quad (22)$$

Thus, the fourth term in Eq. (19) also disappears and Eq. (19) simplifies to

$$\rho_0 \frac{\partial X(\mathbf{P}, \mathbf{F}_e, \hat{\eta})}{\partial \eta} \bigg|_{\mathbf{P}} = \mathbf{P}^t \cdot \mathbf{F}_e \cdot \frac{d^2 \mathbf{U}_t(\hat{\eta})}{d \eta^2} - \rho_0 \frac{\partial^2 \psi^l(\mathbf{E}_e, \hat{\eta})}{\partial \eta^2} \bigg|_{\mathbf{E}_e}. \quad (23)$$

This is our general instability criterion in the concise form.

To find a more explicit form based on the expression (13) for $\rho_0 X$, we first prove that according to Eqs. (15) and (22),

$$\frac{\partial \mathbf{F}(\hat{\eta})}{\partial \eta} \bigg|_{\mathbf{P}} = \mathbf{F}_e \cdot \frac{d \mathbf{U}_t(\hat{\eta})}{d \eta} + \frac{\partial \mathbf{F}_e(\hat{\eta})}{\partial \eta} \bigg|_{\mathbf{P}} \cdot \mathbf{U}_t(\hat{\eta}) = 0. \quad (24)$$

Then, also

$$\frac{\partial J(\hat{\eta})}{\partial \eta} \bigg|_{\mathbf{P}} = \frac{\partial J}{\partial \mathbf{F}^T} \cdot \frac{\partial \mathbf{F}(\hat{\eta})}{\partial \eta} \bigg|_{\mathbf{P}} = 0. \quad (25)$$

Direct differentiation of the driving X in Eq.(13) while allowing for the obtained results leads to the following instability criterion:

$$\rho_0 \frac{\partial X}{\partial \eta} = \mathbf{P}^t \cdot \mathbf{F}_e : \frac{d^2 \mathbf{U}_t(\hat{\eta})}{d\eta^2} - J_t \frac{\partial^2 \psi^e}{\partial \eta^2} \Big|_{\mathbf{F}_e} - J_t \psi^e \mathbf{U}_t^{-1} : \frac{d^2 \mathbf{U}_t}{d\eta^2} - \rho_0 J \frac{\partial^2 \check{\psi}^\theta}{\partial \eta^2} - \rho_0 \frac{\partial^2 \check{\psi}^\theta}{\partial \eta^2} \geq 0, \quad \eta = \hat{\eta}, \quad (26)$$

or in terms of the Cauchy stress:

$$\rho \frac{\partial X}{\partial \eta} = \mathbf{F}_e^t \cdot \boldsymbol{\sigma}_e \cdot \mathbf{F}_e^{t-1} \cdot \mathbf{U}_t^{-1} : \frac{d^2 \mathbf{U}_t}{d\eta^2} - \frac{1}{J_e} \frac{\partial^2 \psi^e}{\partial \eta^2} \Big|_{\mathbf{E}_e} - \frac{\psi^e}{J_e} \mathbf{U}_t^{-1} : \frac{d^2 \mathbf{U}_t}{d\eta^2} - \rho_0 \frac{\partial^2 \check{\psi}^\theta}{\partial \eta^2} - \frac{\rho_0}{J} \frac{\partial^2 \check{\psi}^\theta}{\partial \eta^2} \geq 0, \quad \eta = \hat{\eta}. \quad (27)$$

4.2. Instability of the thermodynamic equilibrium for arbitrary prescribed stresses

Now we prescribe some other stress measure $\tilde{\mathbf{T}}$ (e.g., the Cauchy stress or the second Piola-Kirchoff stress) instead of the first Piola-Kirchoff stress \mathbf{P} . In general, these two stresses are connected through a function $\mathbf{P} = \boldsymbol{\phi}(\tilde{\mathbf{T}}, \mathbf{F}) = \boldsymbol{\phi}_1(\tilde{\mathbf{T}}, \mathbf{F}_e, \mathbf{U}_t(\eta)) = \boldsymbol{\phi}_2(\tilde{\mathbf{T}}, \mathbf{F}_e, \eta)$. Repeating the same procedure but at a fixed $\tilde{\mathbf{T}}$, one obtains the following equation instead of Eq.(18)

$$\rho_0 \frac{\partial X(\tilde{\mathbf{T}}, \mathbf{F}_e, \hat{\eta})}{\partial \eta} \Big|_{\tilde{\mathbf{T}}} \geq 0. \quad (28)$$

An explicit expression for $\frac{\partial X}{\partial \eta} \Big|_{\tilde{\mathbf{T}}}$ will be obtained by direct differentiation of the expression for $\rho_0 X$ from Eq. (14) as follows:

$$\begin{aligned} \rho_0 \frac{\partial X(\tilde{\mathbf{T}}, \mathbf{F}_e, \hat{\eta})}{\partial \eta} \Big|_{\tilde{\mathbf{T}}} &= \frac{\partial \mathbf{P}^t}{\partial \eta} \Big|_{\tilde{\mathbf{T}}} \cdot \mathbf{F}_e : \frac{d \mathbf{U}_t(\hat{\eta})}{d\eta} + \mathbf{P}^t \cdot \frac{\partial \mathbf{F}_e}{\partial \eta} \Big|_{\tilde{\mathbf{T}}} : \frac{d \mathbf{U}_t(\hat{\eta})}{d\eta} + \mathbf{P}^t \cdot \mathbf{F}_e : \frac{d^2 \mathbf{U}_t(\hat{\eta})}{d\eta^2} \\ &- \rho_0 \frac{\partial^2 \psi^l(\mathbf{E}_e, \hat{\eta})}{\partial \eta^2} \Big|_{\mathbf{E}_e} - \rho_0 \frac{\partial^2 \psi^l(\mathbf{E}_e, \hat{\eta})}{\partial \eta \partial \mathbf{F}_e} : \frac{\partial \mathbf{F}_e^t(\hat{\eta})}{\partial \eta} \Big|_{\tilde{\mathbf{T}}}. \end{aligned} \quad (29)$$

The first two terms in Eq. (29) can be eliminated because, based on Eq. (15), $\frac{d \mathbf{U}_t(\hat{\eta})}{d\eta} = 0$.

Let us show that the last term in Eq. (29) can be also eliminated.

(a) Let $\tilde{\mathbf{T}}$ be a nonsymmetric tensor. Then, the thermoelasticity rule has the form $\tilde{\mathbf{T}} = \mathbf{q}(\mathbf{F}_e, \mathbf{U}_t, M^i(\eta))$ with some function \mathbf{q} . Keeping $\tilde{\mathbf{T}} = \text{const}$, we will differentiate this equation with respect to η :

$$0 = \frac{\partial \mathbf{q}}{\partial \mathbf{F}_e^t} \cdot \frac{\partial \mathbf{F}_e(\hat{\eta})}{\partial \eta} \bigg|_{\tilde{\mathbf{T}}} + \frac{\partial \mathbf{q}}{\partial \mathbf{U}_t} \cdot \frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} + \frac{\partial \mathbf{q}}{\partial M^i} \frac{dM^i(\hat{\eta})}{d\eta}. \quad (30)$$

The two last terms in Eq. (30) disappear because of $\frac{dM^i(\hat{\eta})}{d\eta} = 0$ and $\frac{d\mathbf{U}_t(\hat{\eta})}{d\eta} = 0$. Since in general $\det \left(\frac{\partial \mathbf{q}}{\partial \mathbf{F}_e^t} \right) \neq 0$ (with exception for some stress states and measures), nine linear equations (30) with nine unknowns possess the unique solution

$$\frac{\partial \mathbf{F}_e(\hat{\eta})}{\partial \eta} \bigg|_{\tilde{\mathbf{T}}} = 0. \quad (31)$$

Since the last term in Eq. (29) is eliminated, this proves that the instability criterion Eq. (23) is valid for any prescribed stress measure.

(b) Let $\tilde{\mathbf{T}}$ be a symmetric tensor, e.g., the Cauchy stress tensor $\boldsymbol{\sigma}$. In this case Eq. (30) contains six linear algebraic equations only for nine unknowns. This is not unexpected because the rigid-body rotation is not excluded. Similar to the solution of the boundary-value problems we impose three scalar kinematic constraints $\mathbf{j}(\mathbf{F}) = \mathbf{j}(\mathbf{F}_e \cdot \mathbf{U}_t) = \text{const}$, e.g., exclude three shear strains (like in MD simulations in Levitas et al. (2017b)):

$$F_{21} = \{\mathbf{F}_e \cdot \mathbf{U}_t\}_{21} = 0, \quad F_{23} = \{\mathbf{F}_e \cdot \mathbf{U}_t\}_{23} = 0, \quad F_{31} = \{\mathbf{F}_e \cdot \mathbf{U}_t\}_{31} = 0. \quad (32)$$

The differential form of these constraints is

$$0 = \frac{\partial \mathbf{j}}{\partial \mathbf{F}_e^T} \cdot \frac{\partial \mathbf{F}_e(\hat{\eta})}{\partial \eta} + \frac{\partial \mathbf{j}}{\partial \mathbf{U}_t} \cdot \frac{d\mathbf{U}_t(\hat{\eta})}{d\eta}. \quad (33)$$

As was already stated multiple times, the second term disappears. Because the determinant of nine linear algebraic equations (30) and (33) is not zero in a general case, we arrive again at Eq. (22). Thus, again the last term in Eq. (29) disappears, and we obtain the instability criterion Eq. (23) for any prescribed stress measure.

Validity of equations (26) and (27) for arbitrary prescribed stresses can be proven in the same way. Note that it is well known (Hill and Milstein (1977); Milstein et al. (1995)) that the instability criterion depends on the loading device, i.e., the boundary conditions. That is why our result sounds very counterintuitive. However, it is based on additional conditions (15), which resolve the contradiction. We will study this problem in more detail in part II of the paper (Levitas (2018)).

Remark. The question arises: since instability is considered for homogeneous states, for which interfaces and interfacial stresses are absent, why it is important to include interfacial stresses in the instability condition? Interfacial stresses are introduced by making some modifications in the gradient energy ψ^∇ and multiplying $\check{\psi}^\theta + \psi^\nabla$ by the Jacobian determinant J , see Eqs.(6) and (8). For the homogeneous states $\psi^\nabla = 0$. However, the local term $J\check{\psi}^\theta$ remains and contains the Jacobian determinant J , which was absent for the case without interfacial stresses and may affect the instability condition.

4.3. Properties of the interpolation functions related to instability conditions

Conditions for thermodynamic instability of equilibrium phases P_0 and P_1 Eq. (26) should reproduce actual instability criteria obtained e.g., with the help of atomistic simulations or experiments. In general, this means that the second derivative of all interpolation functions participating in Eq. (26) should be controlled, i.e., equal to the prescribed values:

$$\frac{d^2\varphi_m(0)}{d\eta^2} = 2a_m \geq 0; \quad \frac{d^2\varphi_m(1)}{d\eta^2} = 2w_m \leq 0. \quad (34)$$

Since any interpolation function can be presented as the sum of monotonous and double well barrier functions, we will treat them separately. We will start with monotonous interpolation functions; that is why the second derivatives have signs shown in Eq. (11).

5. Examples of interpolation functions

The smallest degree potential that satisfies all the above formulated conditions (11), (12), (16), and (34) is the fifth degree. Thus, starting with the full fifth degree polynomial and applying conditions 1-3, one obtains:

$$\varphi(a, w, \eta) = a\eta^2 + (10 - 3a + w)\eta^3 + (3a - 2w - 15)\eta^4 + (6 - a + w)\eta^5, \quad (35)$$

where subscripts are omitted. This function for different parameters a and w is shown in Fig. 1(a).

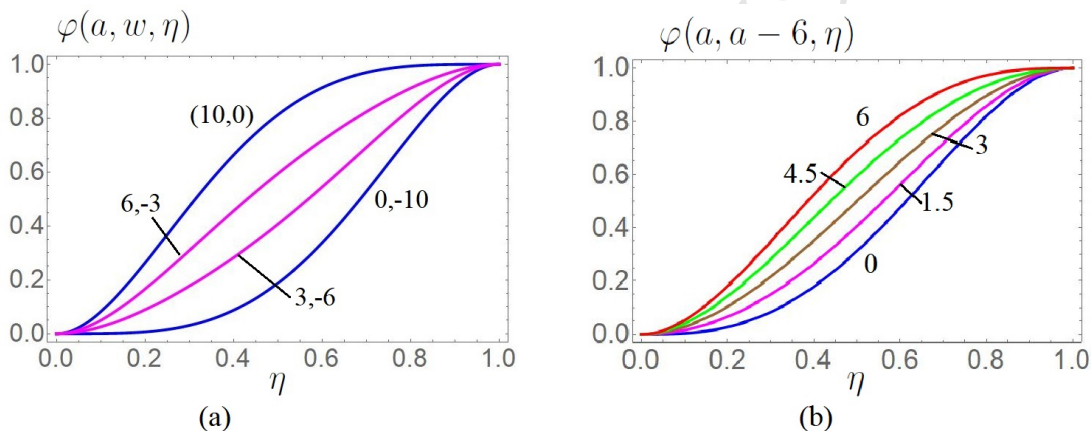


Figure 1: Fifth-degree interpolation function $\varphi(a, w, \eta) = a\eta^2 + (10 - 3a + w)\eta^3 + (3a - 2w - 15)\eta^4 + (6 - a + w)\eta^5$ for several parameters a and w (a) and its particular case a fourth-degree interpolation function $\varphi(a, a - 6, \eta) = a\eta^2(1 - \eta)^2 + \eta^3(4 - 3\eta)$ (b) for several parameters a .

Let us consider different particular cases of this function.

Interpolation function that satisfy antisymmetry condition. If the magnitude of the second derivatives at $\eta = 0$ and 1 is the same, i.e., $w = -a$, interpolation function $\varphi(a, w, \eta)$ reduces to

$$\varphi(a, -a, \eta) = \eta^2[a + (10 - 4a)\eta + 5(a - 3)\eta^2 - 2(a - 3)\eta^3]. \quad (36)$$

It is easy to check that this function satisfies the following antisymmetry condition

$$\varphi(a, -a, 1 - \eta) = 1 - \varphi(a, -a, \eta). \quad (37)$$

This condition imposes an equivalence of phases P_1 and P_0 in the following sense. Let us introduce the order parameter $\bar{\eta} = 1 - \eta$, which is 1 for P_0 and zero for P_1 . Then the interpolation function

$$\varphi(a, -a, \bar{\eta}) = \varphi(a, -a, 1 - \eta) = 1 - \varphi(a, -a, 1 - \bar{\eta}) \quad (38)$$

satisfies the same antisymmetry condition in terms of $\bar{\eta}$. The plot of functions $\varphi(a, -a, \bar{\eta})$ and $\varphi(a, -a, \eta)$ (Fig. 2) is symmetric with respect to the vertical line at $\eta = \bar{\eta} = 0.5$. For large $a = 15$ there is a plateau around $\eta = 0.5$ with the value $\varphi \simeq 0.5$, which can be used to represent an intermediate phase. For dislocations (Levitas et al. (2003)) such a plateau may correspond to the partial dislocation.

Substituting $\eta = 1 - \bar{\eta}$ in Eq.(11) we obtain

$$\begin{aligned} M(\eta, \theta) &= M_0 + (M_1 - M_0)\varphi(a, -a, 1 - \bar{\eta}) = M_0 + (M_1 - M_0)(1 - \varphi(a, -a, \bar{\eta})) \\ &= M_1 + (M_0 - M_1)\varphi(a, -a, \bar{\eta}). \end{aligned} \quad (39)$$

Consequently, material property M is invariant with respect to exchange $(P_0, \eta) \leftrightarrow (P_1, \bar{\eta})$. This condition is not mandatory but allows some simplifications and specification. However, it is required for a multiphase system described by multiple order parameters in theories (Folch and Plapp (2005); Levitas and Roy (2015, 2016)).

Interpolation function for properties that do not contribute to the instability condition. If some material properties do not contribute to the instability condition for PTs $P_0 \rightarrow P_1$ or $P_1 \rightarrow P_0$, then either $a = 0$ or $w = 0$ and one obtains from Eq.(35)

$$\varphi(0, w, \eta) = (10 + w) \eta^3 - (2w + 15) \eta^4 + (6 + w) \eta^5 = \eta^3(w(1 - \eta)^2 + 10 + 3\eta(2\eta - 5)), \quad (40)$$

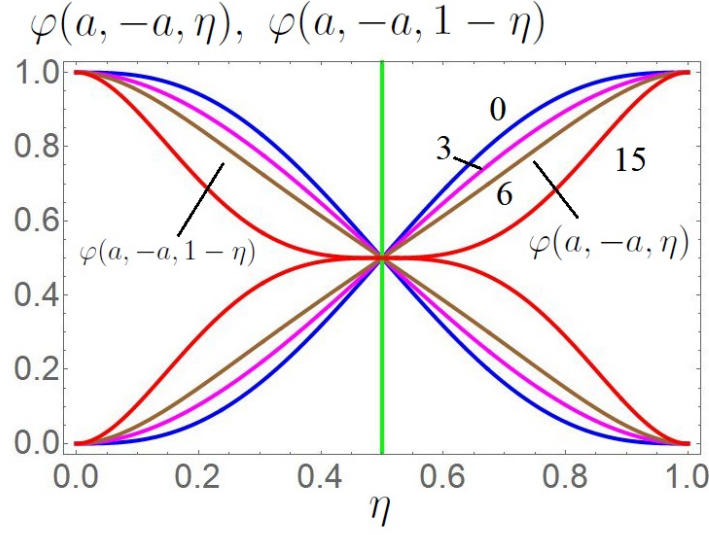


Figure 2: Fifth-degree interpolation functions $\varphi(a, -a, \eta)$ and $\varphi(a, -a, 1 - \eta)$ which satisfy the antisymmetry condition for several parameters a . These functions are symmetric with respect to the vertical line at $\eta = 0.5$.

$$\varphi(a, 0, \eta) = a\eta^2 + (10 - 3a)\eta^3 + (3a - 15)\eta^4 + (6 - a)\eta^5 = \eta^2(a(1 - \eta)^3 + \eta(10 + 3(2\eta - 5))). \quad (41)$$

When both direct and reverse PTs are not affected by some material property, then the corresponding interpolation function looks as

$$\varphi(0, 0, \eta) = \eta^3(10 - 15\eta + 6\eta^2), \quad (42)$$

which also satisfies the antisymmetry condition (37), see Fig. 2. This interpolation function is widely used for the thermal part of the free energy in order to satisfy the phase stability condition for any thermal driving force (Folch and Plapp (2003, 2005); Wang et al. (1993b)). This is nonphysical but serves some purpose for allowing to artificially increase an interface width by reducing the energy barrier between phases. On the other hand, it was found in MD simulations for PTs Si I \leftrightarrow Si II (Levitas et al. (2017a,b)) that the term due to change in elastic moduli (which is nonlinear in stresses) does not contribute to the instability criterion, which was found to be linear in components of the stress tensor. Thus, function (42) have

to be used for elastic moduli tensor of any order.

Fourth-degree interpolation function. A disadvantage of the fifth-degree interpolation function is that it generally does not allow an analytical solution for a propagating interface and, consequently, correct introduction of the interfacial stresses. The only way to reduce the polynomial degree down to fourth is to assume $w = a - 6$ and obtain

$$\varphi(a, a - 6, \eta) = a\eta^2(1 - \eta)^2 + \eta^3(4 - 3\eta). \quad (43)$$

This function for different parameters a is shown in Fig. 1(b). Such an interpolation function was used in Levitas (2013a); Levitas and Preston (2002a,b) for transformation strain. To satisfy the antisymmetry condition (37) one must impose $a = 6 - a$, i.e., $a = 3$ and obtain

$$\varphi(3, -3, \eta) = 3\eta^2(1 - \eta)^2 + \eta^3(4 - 3\eta) = \eta^2(3 - 2\eta). \quad (44)$$

This function, which does not have any fitting parameter, was utilized in Levitas and Roy (2015, 2016) for developing multiphase theory. The fifth degree polynomial (36) that satisfies the antisymmetry condition (37) is much more flexible, because it contains a material parameter a .

Monotonous interpolation function. If properties vary monotonously between phases, then the interpolation function (35) $\varphi(a, w, \eta)$ does not have an extremum on the interval $0 \leq \eta \leq 1$, which impose a constraint on a and w . Condition of the absence of unphysical extrema in the range $0 \leq \eta \leq 1$ for the function (35) can be expressed in terms of quadratic inequalities for a and w . Inequalities

$$a_m \geq 0; \quad w_m \leq 0 \quad (45)$$

are evident necessary but not sufficient conditions.

The above property is directly related to another requirement that the driving force X should not possess unphysical zeros for $0 \leq \eta \leq 1$ for any stresses and temperature. In

particular this means that the Helmholtz free energy should not possess unphysical minima for temperature. Any $0 < \eta < 1$ for which $X = 0$ and $\frac{\partial X}{\partial \eta} < 0$ represents a spurious (unphysical) stable phase. Such η cannot be interpreted as a "discovery" of a new phase since this is just a consequence of the chosen approximation function rather than physically-based knowledge. In particular, one may "reveal" numerous phases by adding some periodic function of the order parameters to the interpolation functions.

When material property is described by a tensor, different a and w in the interpolation function can be applied for each tensorial component. Traditionally they were used the same for all components, see Levitas (2013a); Levitas and Preston (2002a,b). However, based on the results of molecular dynamic simulations for PTs Si I \leftrightarrow Si II in Levitas et al. (2017a,b) (Figs. 4 and 5), different parameters should be used for different components of the transformation strain tensor. We will utilize this in the current paper.

6. Functions for double-well barriers

Using the same reasoning, we conclude that the functions for double-well barriers χ_m satisfy the following conditions

$$\chi_m(0) = 0, \quad \chi_m(1) = 0; \quad (46)$$

$$\frac{d\chi_m(0)}{d\eta} = \frac{d\chi_m(1)}{d\eta} = 0. \quad (47)$$

$$\frac{\partial^2 \chi_m(0)}{\partial \eta^2} = 2A_m; \quad \frac{\partial^2 \chi_m(1)}{\partial \eta^2} = 2Z_m. \quad (48)$$

The minimum degree polynomial that satisfies these conditions is

$$\chi(A, Z, \eta) = (A\eta + Z(1 - \eta))\eta^2(1 - \eta)^2 = (A + Z) \left(\frac{A}{A + Z}\eta + \left(1 - \frac{A}{A + Z}\right)(1 - \eta) \right) \eta^2(1 - \eta)^2. \quad (49)$$

Function $\bar{\chi}(b, \eta) := (b\eta + (1 - b)(1 - \eta))\eta^2(1 - \eta)^2$ for different parameters $b = A/(A + Z)$ is shown in Fig. 3. Traditionally, $A = Z$, which leads to the traditional fourth-degree

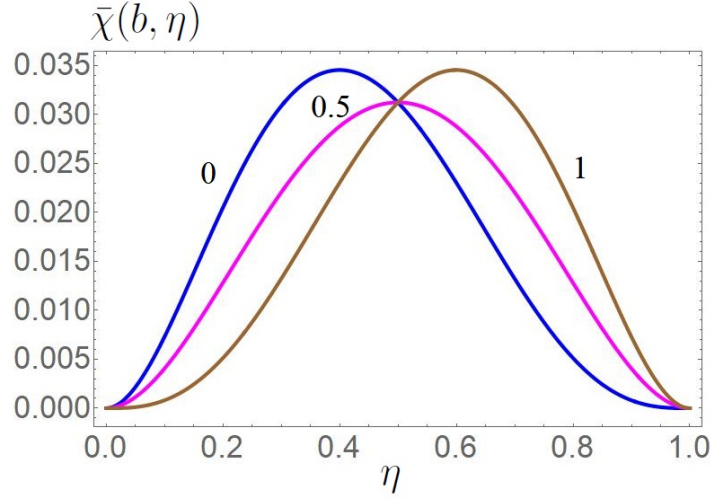


Figure 3: Double well barrier function $\bar{\chi}(b, \eta) = (b\eta + (1 - b)(1 - \eta))\eta^2(1 - \eta)^2$ for different parameters b shown near the curves.

polynomial

$$\chi(A, A, \eta) = A\eta^2(1 - \eta)^2, \quad (50)$$

which is symmetric with respect to $\eta = 0.5$. Different A and Z allow to reproduce asymmetric double-well barrier and different contributions to the instability conditions at $\eta = 0$ and 1 .

7. Thermal part of the free energy and lattice instability conditions for stress-free case

7.1. Fifth-degree polynomial

The most general expression for the thermal part of the free energy that satisfies all of the above conditions can be obtained by combining Eq.(35) for the jump in thermal energy $\Delta\psi^\theta = \psi_1^\theta(\theta) - \psi_0^\theta(\theta)$, where ψ_i^θ is the thermal energy of the bulk phase i , and Eq.(49) for

the double-well barrier:

$$\begin{aligned} \psi^\theta(\theta, \eta) = & \psi_0^\theta(\theta) + \Delta\psi^\theta(\theta)[a\eta^2 + (10 - 3a + w)\eta^3 + (3a - 2w - 15)\eta^4 + (6 - a + w)\eta^5] \\ & + (A\eta + Z(1 - \eta))\eta^2(1 - \eta)^2. \end{aligned} \quad (51)$$

Conditions for thermodynamic instability (23) of equilibrium phases P_0 and P_1 for stress-free conditions should give specific instability temperatures, which are temperatures for barrierless PT or spinodal temperatures. Critical temperature should be below phase equilibrium temperature θ_e for high-temperature phase P_0 and above θ_e for low temperature phase P_1 . Thermodynamic instability conditions (23) for a stress-free case are

$$P_0 \rightarrow P_1 : \quad \frac{\partial X(\theta, 0)}{\partial \eta} = -\frac{\partial^2 \psi^\theta(\theta, 0)}{\partial \eta^2} = -2(A + a\Delta\psi^\theta) \geq 0 \rightarrow -\Delta\psi^\theta \geq \frac{A(\theta)}{a}; \quad (52)$$

$$P_1 \rightarrow P_0 : \quad \frac{\partial X(\theta, 1)}{\partial \eta} = -\frac{\partial^2 \psi^\theta(\theta, 1)}{\partial \eta^2} = -2(Z + w\Delta\psi^\theta) \geq 0 \rightarrow -\Delta\psi^\theta \leq \frac{Z(\theta)}{w}, \quad (53)$$

where we took into account that $w < 0$. Thus, barrierless direct PT $P_0 \rightarrow P_1$ occurs when the driving force $-\Delta\psi^\theta$ exceeds some positive threshold and barrierless reverse PT $P_1 \rightarrow P_0$ occurs when the driving force $-\Delta\psi^\theta$ is smaller than some negative threshold; there is a hysteresis, which is logical.

Let us assume that A , Z and $\Delta\psi^\theta$ are linear functions of temperature:

$$A(\theta) = A_*\theta - B_*; \quad Z(\theta) = Z_*\theta - C_*; \quad \Delta\psi^\theta = -\Delta s(\theta - \theta_e), \quad (54)$$

where A_* , $B_* < 0$, Z_* , and $C_* < 0$ are parameters, and $\Delta s = s_1 - s_0$ is the jump in entropy between phases P_1 and P_0 . We also assume that P_0 is the high-temperature phase and, consequently, $\Delta s < 0$. The linear temperature dependence of $\Delta\psi^\theta$ implies neglecting the difference between specific heats of phases. Then instability conditions (52)-(53) reduce to

$$P_0 \rightarrow P_1 : \quad \theta < \theta_c^0; \quad \theta_c^0 := \frac{a\Delta s \theta_e - B_*}{a\Delta s - A_*}; \quad a\Delta s < A_*; \quad (55)$$

$$P_1 \rightarrow P_0 : \quad \theta > \theta_c^1; \quad \theta_c^1 := \frac{-w\Delta s \theta_e + C_*}{-w\Delta s + Z_*}; \quad w\Delta s < Z_*, \quad (56)$$

where θ_c^0 and θ_c^1 are the critical temperatures for the loss of the thermodynamic stability of phases P_0 and P_1 . The required conditions $\theta_c^0 < \theta_e$ and $\theta_c^1 > \theta_e$ lead to the following constraints: $B < A_*\theta_e$ and $C > Z_*\theta_e$. Since critical temperatures are often not well-known, one of the plausible assumptions, $\theta_e = 0.5(\theta_c^0 + \theta_c^1)$, is used (Levitas and Preston (2002a)). It results in the following constraint

$$(a\Delta s\theta_e - B_*)/(a\Delta s - A_*) + (-w\Delta s\theta_e + C_*)/(-w\Delta s + Z_*) = 2\theta_e. \quad (57)$$

7.2. Fourth-degree polynomial

The problem with Eq.(51) is that we cannot find an analytical solution for a propagating interface and, consequently, correct expression for interfacial stresses. One needs to eliminate the terms with η^5 to be able to complete the theory. Then, a simplified version of Eq.(51) is obtained by placing $w = a - 6$ and $A = Z$:

$$\psi^\theta(\theta, \eta) = \psi_0^\theta(\theta) + (a\Delta\psi^\theta(\theta) + A)\eta^2(1 - \eta)^2 + \Delta\psi^\theta(\theta)\eta^3(4 - 3\eta). \quad (58)$$

This function was used in Levitas and Roy (2016). The instability conditions (52)-(53) simplify to

$$P_0 \rightarrow P_1 : \quad -\Delta\psi^\theta \geq A(\theta)/a; \quad P_1 \rightarrow P_0 : \quad -\Delta\psi^\theta \leq A(\theta)/(a - 6), \quad (59)$$

and the instability conditions (55)-(56) reduce to

$$P_0 \rightarrow P_1 : \quad \theta < \theta_c^0; \quad \theta_c^0 := \frac{a\Delta s\theta_e - B_*}{a\Delta s - A_*}; \quad a\Delta s < A_*; \quad (60)$$

$$P_1 \rightarrow P_0 : \quad \theta > \theta_c^1; \quad \theta_c^1 := \frac{(6 - a)\Delta s\theta_e + B_*}{(6 - a)\Delta s + A_*}; \quad (a - 6)\Delta s < A_*. \quad (61)$$

The conditions $\theta_c^0 < \theta_e$ and $\theta_c^1 > \theta_e$ both lead to the same inequality $B < A_*\theta_e$. An assumption $\theta_e = 0.5(\theta_c^0 + \theta_c^1)$ leads to two possible solutions. The first one, $A_* = B_*/\theta_e$,

results in unphysical relationship $\theta_e = \theta_c^0 = \theta_c^1$. The second second is $A_* = (a - 3)\Delta s$ leading to

$$\theta_c^0 := (a\Delta s \theta_e - B_*)/(3\Delta s); \quad \theta_c^1 := ((6 - a)\Delta s \theta_e + B_*)/(3\Delta s). \quad (62)$$

Thus, the fourth-degree polynomial for ψ^θ has sufficient flexibility to incorporate the desired lattice instability temperatures for a stress-free case. If one additionally imposes the antisymmetry condition (37), then $a = 3$ and instability conditions reduce to

$$P_0 \rightarrow P_1 : \quad -\Delta\psi^\theta \geq A(\theta)/3; \quad P_1 \rightarrow P_0 : \quad -\Delta\psi^\theta \leq -A(\theta)/3. \quad (63)$$

The critical temperatures are

$$\theta_c^0 := (3\Delta s \theta_e - B_*)/(3\Delta s - A_*); \quad \theta_c^1 := (3\Delta s \theta_e + B_*)/(3\Delta s + A_*), \quad (64)$$

and for the case when $\theta_e = 0.5(\theta_c^0 + \theta_c^1)$ one has $A_* = 0$, A is temperature independent, and

$$\theta_c^0 := \theta_e - B_*/(3\Delta s); \quad \theta_c^1 := \theta_e + B_*/(3\Delta s). \quad (65)$$

Eq.(58) for $a = 3$ simplifies to

$$\psi^\theta(\theta, \eta) = \psi_0^\theta(\theta) + \Delta\psi^\theta(\theta)\eta^2(3 - 2\eta) + A\eta^2(1 - \eta)^2. \quad (66)$$

7.3. Analytical solution for a propagating interface and determining functions $\check{\psi}^\theta$ and $\tilde{\psi}^\theta$ in Eq.(6)

The Ginzburg-Landau equation (5) for a stress-free case and one dimensional formulation is

$$\dot{\eta} = LX = L \left(-\frac{\partial\psi^\theta(\theta, \eta)}{\partial\eta} + \beta \frac{d^2\eta}{dx^2} \right). \quad (67)$$

An analytical solution for the propagating interface within a fourth-degree polynomial was obtained in Levitas (2013b) for the particular case of Eq.(58) with $a = 0$. Thus, substituting the magnitude of the double well barrier A in the solution from Levitas (2013b) with

$a\Delta\psi^\theta(\theta) + A$ from Eq.(58), we can trivially generalize analytical solutions in Levitas (2013b) for our model. Thus, for a propagating interface

$$\eta_{in} = (1 + e^{-\zeta})^{-1}; \quad \zeta = k(x - ct); \quad c = 6L\Delta\psi^\theta(\theta)/k; \quad (68)$$

where c is the interface velocity and parameter

$$k = \sqrt{\frac{2(A(\theta) + (a-3)\Delta\psi^\theta(\theta))}{\beta}}; \quad \delta = \frac{10}{k} \quad (69)$$

is proportional to the inverse interface width, δ . Note that different definitions of the interface width results in a different proportionality factor (Levitas et al. (2010, 2003)). The temperature at which the propagating interface exists is constrained by the existence of a real-valued k , i.e., $A(\theta) > (3-a)\Delta\psi^\theta(\theta)$. One of the important properties of solution Eq.(68) is

$$d\eta_{in}/d\zeta = \eta_{in}(1 - \eta_{in}). \quad (70)$$

Using it and the definition of k in Eq.(69), we obtain an important relationship for the points of a propagating interface:

$$\psi^\nabla = \frac{\beta}{2} |\nabla \eta_{in}|^2 = \frac{\beta k^2}{2} \left(\frac{d\eta_{in}}{d\zeta} \right)^2 = [A(\theta) + (a-3)\Delta\psi^\theta(\theta)] \eta_{in}^2 (1 - \eta_{in})^2. \quad (71)$$

Repeating the same steps as in Levitas (2013b) we obtain a splitting of the general fourth-degree polynomial in Eq.(58) into the part that according to Eq.(6) contributes to the interfacial stresses

$$\check{\psi}^\theta := [A(\theta) + (a-3)\Delta\psi^\theta(\theta)] \eta^2 (1 - \eta)^2, \quad (72)$$

and the remaining part, which does not participate in the interfacial stresses

$$\tilde{\psi}^\theta = \psi^\theta(\theta, \eta) - \check{\psi}^\theta = \Delta\psi^\theta(\theta) \eta^2 (3 - 2\eta) + \psi_0^\theta(\theta). \quad (73)$$

Eq.(72) for $a = 0$ reduces to the expression for $\check{\psi}^\theta$ in Levitas (2013b). Similar to Levitas (2013b, 2014b), the Gibbsian divided surfaces for the propagating interface passes through the point with $\eta = 0.5$. For $a = 3$ one obtains $\check{\psi}^\theta = A(\theta)\eta^2(1 - \eta)^2$ and expressions for the interface stresses, width, and energy are independent of the thermal driving force $\Delta\psi^\theta$, like in Levitas and Roy (2016); Steinbach (2009). Analyzing Eq.(72), the main problem in determining $\check{\psi}^\theta$ can be reformulated: which part of ψ^θ proportional to the thermal driving force $\Delta\psi^\theta$ contributes to the double-well function? A priori answer is not unique, because instead of $3 - a$ one can use an arbitrary multiplier, which will change $\check{\psi}^\theta$. The notable property of the obtained solution Eqs.(72) and (73) is that the maximum degree of $\check{\psi}^\theta$ reduced in comparison with that of ψ^θ . The same is true for the sixth-degree polynomial in Levitas (2014b).

8. Expressions for transformation strain and stress-related contributions to the thermodynamic driving force and instability conditions

8.1. Interpolation for transformation strain $\boldsymbol{\varepsilon}_t := \mathbf{U}_t - \mathbf{I}$

For each component of the transformation strain tensor $\boldsymbol{\varepsilon}_t = \varepsilon_t^{ij}(\eta)\mathbf{e}_i \otimes \mathbf{e}_j$, where \mathbf{e}_j is the Cartesian unit basis vector, we accept the general fifth-degree approximation as in Eq.(35) plus additional terms:

$$\begin{aligned} \varepsilon_t^{ij}(\eta) &= \varepsilon_t^{ij}(0) + \Delta\varepsilon_t^{ij}\varphi^{ij} + A_\varepsilon^{ij}\bar{\phi}; & \bar{\phi} &:= \eta^2(1 - \eta)^2 \\ \varphi^{ij} &:= [a_\varepsilon^{ij}\eta^2 + (10\iota^{ij} - 3a_\varepsilon^{ij} + w_\varepsilon^{ij})\eta^3 + (3a_\varepsilon^{ij} - 2w_\varepsilon^{ij} - 15\iota^{ij})\eta^4 + (6\iota^{ij} - a_\varepsilon^{ij} + w_\varepsilon^{ij})\eta^5]. \end{aligned} \quad (74)$$

Here, matrix φ^{ij} (and, consequently, matrices a_ε^{ij} , w_ε^{ij} , and ι_ε^{ij}) have the same non-zero components and symmetry as $\Delta\varepsilon_t^{ij}$; non-zero components of ι^{ij} are equal to unity, and no summation is performed over the repeating superscripts. In the previous theories (Levitas (2013a); Levitas and Preston (2002a,b); Levitas et al. (2003)) all components of the $\Delta\varepsilon_t^{ij}$ are

multiplied by the same function $\varphi^{ij} = \varphi$ (i.e., $a_\varepsilon^{ij} = a_\varepsilon$ and $w_\varepsilon^{ij} = w_\varepsilon$ for all i, j) and $A_\varepsilon^{ij} = 0$, i.e.,

$$\begin{aligned}\varepsilon_t^{ij}(\eta) &= \varepsilon_t^{ij}(0) + \Delta\varepsilon_t^{ij}\varphi; & \boldsymbol{\varepsilon}_t(\eta) &= \boldsymbol{\varepsilon}_t(0) + \Delta\varepsilon_t\varphi; \\ \varphi &:= [a_\varepsilon\eta^2 + (10 - 3a_\varepsilon + w_\varepsilon)\eta^3 + (3a_\varepsilon - 2w_\varepsilon - 15)\eta^4 + (6 - a_\varepsilon + w_\varepsilon)\eta^5].\end{aligned}\tag{75}$$

In this case, all nonzero components of the transformation strain tensor vary proportionally to a single order parameter and if some of the components of the transformation strain tensor are zero after complete PT, they do not appear and disappear during transformation, and do not affect the driving force for PT and lattice instability conditions. However, such a version could not reproduce instability conditions obtained with MD simulations in Levitas et al. (2017a,b).

Eq.(74) utilizes different constants a_ε^{ij} and w_ε^{ij} for each independent component of the transformation strain tensor. In this case the transformation strain path in the space of the transformation strain tensor components represents some curved line connecting initial and final values. This generalization is sufficient for the description of the instability conditions obtained with MD simulations in Levitas et al. (2017a,b), see Section 9.

Let us discuss the additional terms $A_\varepsilon^{ij}\eta^2(1 - \eta)^2$, which without problem can be substituted in all following equations with the more general interpolation function Eq.(49). For most PTs, some components of the transformation strain tensor $\boldsymbol{\varepsilon}_t(1)$ are zero. The components A_ε^{ij} are nonzero for those i and j for which $\Delta\varepsilon_t^{ij} = 0$ only. For example, for cubic to tetragonal PT $\boldsymbol{\varepsilon}_t(1)$ has nonzero diagonal components only in the coordinate system of the cubic cell. Thus, the terms $A_\varepsilon^{ij}\eta^2(1 - \eta)^2$ are off-diagonal and show an increase and then a disappearance of the transformation shear strains. The terms $A_\varepsilon^{ij}\eta^2(1 - \eta)^2$ contributes to the instability condition when corresponding stresses are acting. Thus, they are introduced to include a possible effect on the instability conditions of stresses which do not produce transformation work with $\boldsymbol{\varepsilon}_t(1)$ and, consequently, do not contribute to the phase equilib-

rium conditions, as well as to include a transformation path more complex than described by $\boldsymbol{\varepsilon}_t(1)$. For example, shear stresses for cubic to tetragonal PT change symmetry of the lattice and may affect elastic lattice instability.

For compactness, we rewrite this equation in the index-free form:

$$\boldsymbol{\varepsilon}_t(\eta) = \boldsymbol{\varepsilon}_t(0) + \Delta\boldsymbol{\varepsilon}_t \circ \boldsymbol{\varphi} + \mathbf{A}_\varepsilon \eta^2 (1 - \eta)^2, \quad (76)$$

where $\mathbf{A}_\varepsilon := \{A_\varepsilon^{ij}\}$ is the tensor and we define the Hadamard product of matrix $\Delta\boldsymbol{\varepsilon}_t \circ \boldsymbol{\varphi} := \{\Delta\varepsilon_t^{ij} \varphi^{ij}\}$ (note no summation over i and j) and corresponding tensor $\Delta\boldsymbol{\varepsilon}_t \circ \boldsymbol{\varphi} := \Delta\varepsilon_t^{ij} \varphi^{ij} \mathbf{e}_i \otimes \mathbf{e}_j$. Note that $\Delta\boldsymbol{\varepsilon}_t \circ \boldsymbol{\varphi} := \{\Delta\varepsilon_t^{ij} \varphi^{ij}\}$ should not be confused with a scalar double contraction of two tensors with components $\Delta\varepsilon_t^{ij}$ and φ^{ij} ; this is tensor $\Delta\boldsymbol{\varepsilon}_t$ each component $\Delta\varepsilon_t^{ij}$ of which is multiplied by a scalar φ^{ij} . Note that

$$\boldsymbol{\varphi} := [\mathbf{a}_\varepsilon \eta^2 + (10\boldsymbol{\iota} - 3\mathbf{a}_\varepsilon + \mathbf{w}_\varepsilon) \eta^3 + (3\mathbf{a}_\varepsilon - 2\mathbf{w}_\varepsilon - 15\boldsymbol{\iota}) \eta^4 + (6\boldsymbol{\iota} - \mathbf{a}_\varepsilon + \mathbf{w}_\varepsilon) \eta^5] \quad (77)$$

and, consequently, $\mathbf{a}_\varepsilon := \{a_\varepsilon^{ij}\}$, $\mathbf{w}_\varepsilon := \{w_\varepsilon^{ij}\}$, and $\boldsymbol{\iota}$, are matrices but not second-rank tensors, because they do not transform as tensors under change of basis. That is why they should be defined in some special basis, e.g., in the basis corresponding to the parent crystal lattice or cubic lattice, or in the principle basis. Tensorial transformations to different bases can be performed for $\{\Delta\varepsilon_t^{ij}\}$ and $\{\Delta\varepsilon_t^{ij} \varphi^{ij}\}$ only, but not for $\{\varphi^{ij}\}$.

Below we evaluate the transformational Jacobian determinant, which is the volumetric deformation transformation gradient:

$$J_t(\eta) = \det \mathbf{U}_t(\eta) = \det [\mathbf{I} + \boldsymbol{\varepsilon}_t(0) + \Delta\boldsymbol{\varepsilon}_t \circ \boldsymbol{\varphi} + \mathbf{A}_\varepsilon \eta^2 (1 - \eta)^2]. \quad (78)$$

In the simplest case $\boldsymbol{\varepsilon}_t(0) = 0$, $\mathbf{A}_\varepsilon = 0$, and all $\varphi^{ij} = \varphi$ are the same, Eq.(78) simplifies to

$$J_t(\eta) = \det [\mathbf{I} + \Delta\boldsymbol{\varepsilon}_t \varphi(\eta)] = \prod [1 + \Delta\varepsilon_t^{ii} \varphi(\eta)], \quad (79)$$

where $\Delta\varepsilon_t^{ii}$ are the principle components of the tensor $\Delta\boldsymbol{\varepsilon}_t$. For small strains,

$$J_t(\eta) - 1 = \sum \Delta\varepsilon_t^{ii} \varphi(\eta) = (J_t(1) - 1) \varphi(\eta), \quad (80)$$

i.e., the volumetric transformation strain $J_t(\eta) - 1$ is expressed in terms of its final value $J_t(1) - 1$ and an interpolation function $\varphi(\eta)$, and for $J_t(1) = 1$ one has $J_t(\eta) = 1$ for all η . In contrast, for finite strains, even for the simplest case in Eq.(79), this is impossible. I.e., variation of the volumetric transformation strain $J_t(\eta) - 1$ cannot be expressed in terms of its final value $J_t(1) - 1$ and some interpolation function. In particular, if $J_t(1) = 1$, i.e. product crystal cell has the same specific volume as the parent one, which is true for twinning, transformation between martensitic variants, and approximately the case for some shape memory alloys, one would expect that all intermediate states also have the same specific volume. However, it does not follow from Eq.(79) that $J_t(\eta) = 1$.

8.2. Stress and transformation strain related contributions to the driving force X and instability conditions

Let us evaluate stress power in the driving force X in Eq.(10)

$$\mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1} \cdot \frac{d\mathbf{U}_t(\eta)}{d\eta} = \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} \cdot \mathbf{U}_t^{-1} : \left\{ \Delta \boldsymbol{\varepsilon}_t \circ \frac{d\boldsymbol{\varphi}}{d\eta} + \mathbf{A}_\varepsilon \frac{d\bar{\boldsymbol{\phi}}}{d\eta} \right\}. \quad (81)$$

Decomposing the Cauchy stress into a spherical part, i.e., the mean stress, σ_0 , and deviatoric part, $\mathbf{S} = dev \boldsymbol{\sigma}$,

$$\boldsymbol{\sigma} = \sigma_0 \mathbf{I} + \mathbf{S}; \quad \sigma_0 := \frac{1}{3} \boldsymbol{\sigma} : \mathbf{I}; \quad \mathbf{S} = dev \boldsymbol{\sigma}, \quad (82)$$

we elaborate Eq.(81)

$$\mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1} \cdot \frac{d\mathbf{U}_t(\eta)}{d\eta} = \sigma_0 \mathbf{U}_t^{-1} : \frac{d\mathbf{U}_t(\eta)}{d\eta} + \mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : dev \left\{ \mathbf{U}_t^{-1} \cdot \frac{d\mathbf{U}_t(\eta)}{d\eta} \right\}, \quad (83)$$

where we took into account that $\mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1}$ is a deviator, because $\mathbf{I} : \mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} = \mathbf{F}_e^{t-1} \cdot \mathbf{F}_e^t : \mathbf{S} = \mathbf{I} : \mathbf{S} = 0$. Since

$$\mathbf{U}_t^{-1} : \frac{d\mathbf{U}_t(\eta)}{d\eta} = J_t^{-1}(\eta) \frac{dJ_t(\eta)}{d\eta} = \frac{d}{d\eta} \ln \left[\frac{J_t(\eta)}{J_t(0)} \right] \quad (84)$$

is the η -derivative of logarithmic volumetric transformation strain, the first term in the right hand side of Eq.(116) is the transformation power of the change in volume. However, since $J_t(\eta)$ cannot be expressed in terms of $J_t(1)$ and some interpolating function of η , even if $J_t(1) = J_t(0)$, i.e., both phases have the same specific volume in the unloaded state, $J_t(\eta) \neq J_t(0)$ for all η during PT, and the mean stress produces a contribution to the evolution of η . Since for $J_t(1) = J_t(0)$

$$\int_0^1 \frac{d}{d\eta} \ln \left[\frac{J_t(\eta)}{J_t(0)} \right] d\eta = \ln \left[\frac{J_t(1)}{J_t(0)} \right] = 0, \quad (85)$$

the total contribution of the constant mean stress σ_0 to the transformation work when η varies from 0 to 1 disappears. However, volumetric strain produces internal stresses and their total work may not be zero when η varies from 0 to 1.

Next, substituting the expression for $\frac{d\mathbf{U}_t(\eta)}{d\eta}$ from Eq.(81) into Eq.(83), we obtain

$$\begin{aligned} \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1}(\eta) \cdot \frac{d\mathbf{U}_t(\eta)}{d\eta} &= \sigma_0 \mathbf{U}_t^{-1}(\eta) : \left\{ \Delta \boldsymbol{\varepsilon}_t \circ \frac{d\boldsymbol{\varphi}}{d\eta} + \mathbf{A}_\varepsilon \frac{d\bar{\phi}}{d\eta} \right\} + \\ \mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : dev \left\{ \mathbf{U}_t^{-1}(\eta) \cdot \left[\Delta \boldsymbol{\varepsilon}_t \circ \frac{d\boldsymbol{\varphi}}{d\eta} + \mathbf{A}_\varepsilon \frac{d\bar{\phi}}{d\eta} \right] \right\}. \end{aligned} \quad (86)$$

It is difficult to further simplify this expression even when all $\varphi^{ij} = \varphi$ are the same and $diag(\mathbf{A}_\varepsilon) = 0$. Similarly, we evaluate the stress contribution to the instability criterion Eq.(27)

$$\begin{aligned} \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1}(0) \cdot \frac{d^2 \mathbf{U}_t(0)}{d\eta^2} &= \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : 2 (\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{a}_\varepsilon + \mathbf{A}_\varepsilon) = \\ \sigma_0 \mathbf{I} : 2 (\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{a}_\varepsilon + \mathbf{A}_\varepsilon) &+ \mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : 2 dev (\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{a}_\varepsilon + \mathbf{A}_\varepsilon); \end{aligned} \quad (87)$$

$$\begin{aligned} \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1}(1) \cdot \frac{d^2 \mathbf{U}_t(1)}{d\eta^2} &= \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1}(1) \cdot 2 [\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{w}_\varepsilon + \mathbf{A}_\varepsilon] = \\ \sigma_0 \mathbf{U}_t^{-1}(1) : 2 [\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{w}_\varepsilon + \mathbf{A}_\varepsilon] &+ \mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : dev \{ \mathbf{U}_t^{-1}(1) \cdot 2 [\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{w}_\varepsilon + \mathbf{A}_\varepsilon] \}. \end{aligned} \quad (88)$$

Even for scalar a_ε and w_ε and $diag(\mathbf{A}_\varepsilon) = 0$, the multiplier for σ_0 is not related to volumetric transformation strain only. That is why in expressions below we will not split stress contribution to the instability criterion into spherical and deviatoric parts. In fact, matrices \mathbf{a}_ε

and \mathbf{w}_ε may be used to correct this. It is clear that tensor \mathbf{A}_ε allows one to include the effect on the lattice instability condition of the stresses, for which corresponding components of the final transformation strain are absent.

8.3. Interpolation for logarithmic transformation strain $\ln \mathbf{U}_t$

We will try similar interpolation but for logarithmic strain measure:

$$\ln \mathbf{U}_t(\eta) = \ln \mathbf{U}_t(0) + (\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0)) \circ \boldsymbol{\varphi} + \ln(\mathbf{B}_\varepsilon) \bar{\phi}, \quad (89)$$

i.e.,

$$\mathbf{U}_t(\eta) = \exp \{ \ln \mathbf{U}_t(0) + (\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0)) \circ \boldsymbol{\varphi} + \ln(\mathbf{B}_\varepsilon) \bar{\phi} \}, \quad (90)$$

where the components $\ln \mathbf{B}_\varepsilon$ are nonzero for those i and j for which $\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0) = 0$ only. Below, we will use the following identities for a second-rank tensor \mathbf{A} (see Jog (2015)):

$$\det(\exp(\mathbf{A})) = \exp(\text{tr}(\mathbf{A})); \quad \text{tr}(\ln(\mathbf{A})) = \ln(\det \mathbf{A}). \quad (91)$$

Let us evaluate the volumetric deformation transformation gradient, i.e., the transformational Jacobian determinant

$$\begin{aligned} J_t &= \det \mathbf{U}_t(\eta) = \det \{ \exp [\ln \mathbf{U}_t(0) + (\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0)) \circ \boldsymbol{\varphi} + \ln(\mathbf{B}_\varepsilon) \bar{\phi}] \} = \\ &= \exp [\text{tr}(\ln \mathbf{U}_t(0)) + \text{tr}((\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0)) \circ \boldsymbol{\varphi}) + \text{tr}(\ln(\mathbf{B}_\varepsilon)) \bar{\phi}] \\ &= \exp [\ln(\det(\mathbf{U}_t(0))) + \text{tr}((\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0)) \circ \boldsymbol{\varphi}) + \ln(\det(\mathbf{B}_\varepsilon)) \bar{\phi}] = \\ &= \det(\mathbf{U}_t(0)) (\det(\mathbf{B}_\varepsilon))^{\bar{\phi}} \exp \{ \text{tr}[(\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0)) \circ \boldsymbol{\varphi}] \}. \end{aligned} \quad (92)$$

The last multiplier in the component form is

$$\text{tr}[(\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0)) \circ \boldsymbol{\varphi}] = \sum (\ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0))_{ii} \varphi^{ii}, \quad (93)$$

which in general cannot be simplified further. However, for $\eta = 1$ all $\varphi_0^{ii} = \varphi_1^{ii} = 1$,

$$tr(ln\mathbf{U}_t(1) - ln\mathbf{U}_t(0)) = ln(det(\mathbf{U}_t(1)) - ln(det(\mathbf{U}_t(0))) = ln(det(\mathbf{U}_t(1))/(det(\mathbf{U}_t(0))) \quad (94)$$

and

$$exp\{tr[ln\mathbf{U}_t(1) - ln\mathbf{U}_t(0)]\} = det(\mathbf{U}_t(1))/det(\mathbf{U}_t(0)). \quad (95)$$

Also, if all $\varphi^{ij} = \varphi$ are the same, in a similar way we obtain

$$tr[ln\mathbf{U}_t(1) - ln\mathbf{U}_t(0)]\varphi = ln[det(\mathbf{U}_t(1))/det(\mathbf{U}_t(0))]\varphi = ln\left\{\left[\frac{det(\mathbf{U}_t(1))}{det(\mathbf{U}_t(0))}\right]^\varphi\right\}, \quad (96)$$

and

$$exp\{tr[ln\mathbf{U}_t(1) - ln\mathbf{U}_t(0)]\varphi\} = [det(\mathbf{U}_t(1))/det(\mathbf{U}_t(0))]^\varphi. \quad (97)$$

Then

$$J_t = det\mathbf{U}_t(\eta) = det(\mathbf{U}_t(0))(det(\mathbf{B}_\varepsilon))^{\bar{\phi}} \left[\frac{det(\mathbf{U}_t(1))}{det(\mathbf{U}_t(0))}\right]^\varphi. \quad (98)$$

If tensor $ln\mathbf{U}_t(1) - ln\mathbf{U}_t(0)$ has all nonzero diagonal components, then tensor $ln\mathbf{B}_\varepsilon$ has off-diagonal components only and $tr(ln\mathbf{B}_\varepsilon) = 0 \rightarrow ln(det(\mathbf{B}_\varepsilon)) = 0 \rightarrow det(\mathbf{B}_\varepsilon) = 1$. Let us for simplicity assume $\mathbf{U}_t(0) = \mathbf{I}$. Then Eq.(98) reduces to

$$\begin{aligned} J_t(\eta) &= det\mathbf{U}_t(\eta) = (det\mathbf{U}_t(1))^{\varphi(\eta)} = J_t(1)^{\varphi(\eta)}; \\ ln[J_t(\eta)] &= \varphi(\eta)ln[J_t(1)]. \end{aligned} \quad (99)$$

In this case the volumetric transformation gradient $J_t(\eta)$ is expressed in terms of $J_t(1)$ and an interpolation function $\varphi(\eta)$ and for $J_t(1) = 1$ one has $J_t(\eta) = 1$ for all η . This is, however, impossible for different interpolation functions φ^{ij} , i.e., variation of the volumetric transformation gradient $J_t(\eta)$ cannot be expressed in terms of the final value $J_t(1)$ and some interpolation function. In particular, if $J_t(1) = 1$, one would expect that all intermediate states also have the same specific volume. However, it does not follow from Eq.(93) that $J_t(\eta) = 1$. The above particular case gives us an idea on how to modify interpolation Eq.(89) to satisfy this requirement for a more general case.

8.4. Interpolation for logarithmic transformation strain $\ln \mathbf{U}_t$ that separates volumetric and deviatoric parts

We present

$$\ln \mathbf{U}_t(\eta) = \ln \mathbf{U}_t(0) + \mathbf{H}(\eta) + \ln(\mathbf{B}_\varepsilon) \bar{\phi}, \quad (100)$$

with

$$\mathbf{H}(1) = \ln \mathbf{U}_t(1) - \ln \mathbf{U}_t(0); \quad \mathbf{H}(0) = 0. \quad (101)$$

The following interpolation for components of the tensor $\mathbf{H}(\eta)$ is suggested

$$H^{ij}(\eta) = H_v(1) \delta^{ij} \varphi_v(a_v, w_v, \eta) + H_{dd}^{ii}(1) \varphi^{ii}(a_d^{ii}, w_d^{ii}, \eta) + H_{of}^{ij}(1) \varphi^{ij}(a_{of}^{ij}, w_{of}^{ij}, \eta); \quad (102)$$

$$H_v(1) = \frac{1}{3} \sum H^{ii}(1); \quad \sum H_{dd}^{ii}(1) \varphi^{ii}(a_d^{ii}, w_d^{ii}, \eta) = 0 \quad \forall \eta; \quad H_{of}^{ii}(1) \varphi^{ii}(a_{of}^{ii}, w_{of}^{ii}, \eta) = 0. \quad (103)$$

Thus, tensor $\mathbf{H}(\eta)$ consists of a spherical part H_v , which solely determines volumetric transformation strain, and diagonal deviatoric H_{dd}^{ii} and off-diagonal H_{of}^{ij} parts, which do not affect volumetric transformation strain. Condition for the diagonal deviatoric parts can be satisfied for

$$a_d^{33} = \frac{a_d^{11}(H_{dd}^{22}(1) + H_{dd}^{33}(1)) - a_d^{22} H_{dd}^{22}(1)}{H_{dd}^{33}(1)}; \quad w_d^{33} = \frac{w_d^{11}(H_{dd}^{22}(1) + H_{dd}^{33}(1)) - w_d^{22} H_{dd}^{22}(1)}{H_{dd}^{33}(1)} \quad (104)$$

which can be obtained by applying a deviatoric constraint for multipliers for each power η^k , $k = 2, 3, 4, 5$. In the compact form Eqs.(102) and (103) can be presented as

$$\mathbf{H}(\eta) = H_v(1) \mathbf{I} \varphi_v(a_v, w_v, \eta) + \mathbf{H}_{dd}(1) \circ \varphi_{dd}(\mathbf{a}_d, \mathbf{w}_d, \eta) + \mathbf{H}_{of}(1) \circ \varphi_{of}(\mathbf{a}_{of}, \mathbf{w}_{of}, \eta); \quad (105)$$

$$H_v(1) = \frac{1}{3} \text{tr} \mathbf{H}(1) = \frac{1}{3} [\ln(\det \mathbf{U}_t(1)) - \ln(\det \mathbf{U}_t(0))] = \frac{1}{3} \ln \frac{\det \mathbf{U}_t(1)}{\det \mathbf{U}_t(0)} = \frac{1}{3} \ln \frac{J_t(1)}{J_t(0)};$$

$$\text{tr} [\mathbf{H}_{dd}(1) \circ \varphi_{dd}(\mathbf{a}_d, \mathbf{w}_d, \eta)] = 0 \quad \forall \eta; \quad \text{diag} [\mathbf{H}_{of}(1) \circ \varphi_{of}(\mathbf{a}_{of}, \mathbf{w}_{of}, \eta)] = 0. \quad (106)$$

Then,

$$\mathbf{U}_t(\eta) = \exp \left\{ \ln \mathbf{U}_t(0) + \mathbf{H}(\eta) + \ln(\mathbf{B}_\varepsilon) \bar{\phi} \right\}, \quad (107)$$

$$\begin{aligned} J_t(\eta) &= \det \mathbf{U}_t(\eta) = \det \left\{ \exp \left[\ln \mathbf{U}_t(0) + \mathbf{H}(\eta) + \ln(\mathbf{B}_\varepsilon) \bar{\phi} \right] \right\} = \\ &= \exp \left[\text{tr}(\ln \mathbf{U}_t(0)) + \text{tr}(\mathbf{H}(\eta)) + \text{tr}(\ln(\mathbf{B}_\varepsilon) \bar{\phi}) \right] \\ &= \exp \left[\ln(\det(\mathbf{U}_t(0))) + \ln \left(\frac{\det \mathbf{U}_t(1)}{\det \mathbf{U}_t(0)} \right)^{\varphi_v} + \ln(\det(\mathbf{B}_\varepsilon)) \bar{\phi} \right] = \\ &= \det(\mathbf{U}_t(0)) \left(\frac{\det \mathbf{U}_t(1)}{\det \mathbf{U}_t(0)} \right)^{\varphi_v} (\det(\mathbf{B}_\varepsilon))^{\bar{\phi}} = J_t(0) \left(\frac{J_t(1)}{J_t(0)} \right)^{\varphi_v} (\det(\mathbf{B}_\varepsilon))^{\bar{\phi}}. \end{aligned} \quad (108)$$

Thus, for $\det \mathbf{B}_\varepsilon = 1$ (i.e., when $\text{diag}[\ln(\mathbf{B}_\varepsilon)] = 0$), η -variation of the volumetric deformation gradient $J_t(\eta)$ can be expressed in terms of $J_t(1)$, $J_t(0)$, and interpolation function φ_v , as desired. In particular, for the same specific volume of phases $J_t(1) = J_t(0)$ and $J_t(\eta) = J_t(0)$ does not vary during phase transformation. If based on some available data one needs to add variation of volumetric strain in general or for the same specific volume of phases, one has to add a spherical part to $\ln(\mathbf{B}_\varepsilon)$.

Using a Taylor series for the exponential function,

$$\begin{aligned} \mathbf{U}_t(\eta) &= \exp \left\{ \sum \mathbf{A}^i \circ \boldsymbol{\varphi}^i(\eta) \right\} = \mathbf{I} + \sum \mathbf{A}^i \circ \boldsymbol{\varphi}^i(\eta) + \\ &+ \frac{1}{2!} \left\{ \sum \mathbf{A}^i \circ \boldsymbol{\varphi}^i(\eta) \right\}^2 + \frac{1}{3!} \left\{ \sum \mathbf{A}^i \circ \boldsymbol{\varphi}^i(\eta) \right\}^3 + \dots \end{aligned} \quad (109)$$

and differentiating with respect to scalar η , one obtains

$$\frac{d\mathbf{U}_t}{d\eta} = \mathbf{U}_t \cdot \left\{ \sum \mathbf{A}^i \circ \frac{d\boldsymbol{\varphi}^i}{d\eta} \right\}; \quad (110)$$

$$\frac{d^2\mathbf{U}_t}{d\eta^2} = \mathbf{U}_t \cdot \left\{ \sum \mathbf{A}^i \circ \frac{d^2\boldsymbol{\varphi}^i}{d\eta^2} \right\} + \mathbf{U}_t \cdot \left\{ \sum \mathbf{A}^i \circ \frac{d\boldsymbol{\varphi}^i}{d\eta} \right\}^2, \quad (111)$$

where \mathbf{A}^i and $\boldsymbol{\varphi}^i(\eta)$ are η -independent tensors and corresponding interpolation functions in Eq.(107). Since $\frac{d\boldsymbol{\varphi}^i(\hat{\eta})}{d\eta} = 0$, then

$$\frac{d^2\mathbf{U}_t(\hat{\eta})}{d\eta^2} = \mathbf{U}_t \cdot \left\{ \sum \mathbf{A}^i \circ \frac{d^2\boldsymbol{\varphi}^i(\hat{\eta})}{d\eta^2} \right\}. \quad (112)$$

More explicitly,

$$\frac{d\mathbf{U}_t}{d\eta} = \mathbf{U}_t \cdot \left\{ H_v(1)\mathbf{I} \frac{d\varphi_v}{d\eta} + \mathbf{H}_{dd}(1) \circ \frac{d\boldsymbol{\varphi}_{dd}}{d\eta} + \mathbf{H}_{of}(1) \circ \frac{d\boldsymbol{\varphi}_{of}}{d\eta} + \ln(\mathbf{B}_\varepsilon) \frac{d\bar{\phi}}{d\eta} \right\}. \quad (113)$$

$$\frac{d^2\mathbf{U}_t(\hat{\eta})}{d\eta^2} = \mathbf{U}_t \cdot \left\{ H_v(1)\mathbf{I} \frac{d^2\varphi_v(\hat{\eta})}{d\eta^2} + \mathbf{H}_{dd}(1) \circ \frac{d^2\boldsymbol{\varphi}_{dd}(\hat{\eta})}{d\eta^2} + \mathbf{H}_{of}(1) \circ \frac{d^2\boldsymbol{\varphi}_{of}(\hat{\eta})}{d\eta^2} + \ln(\mathbf{B}_\varepsilon) \frac{d^2\bar{\phi}(\hat{\eta})}{d\eta^2} \right\} \quad (114)$$

8.5. Contributions to the driving force X and instability conditions due to stress and transformation strain

Let us evaluate the stress contribution to the driving force X in Eq.(10)

$$\begin{aligned} \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1} \cdot \frac{d\mathbf{U}_t(\eta)}{d\eta} = \\ \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \left\{ H_v(1)\mathbf{I} \frac{d\varphi_v}{d\eta} + \mathbf{H}_{dd}(1) \circ \frac{d\boldsymbol{\varphi}_{dd}}{d\eta} + \mathbf{H}_{of}(1) \circ \frac{d\boldsymbol{\varphi}_{of}}{d\eta} + \ln(\mathbf{B}_\varepsilon) \frac{d\bar{\phi}}{d\eta} \right\}. \end{aligned} \quad (115)$$

Decomposing the Cauchy stress into a spherical part, i.e., the mean stress, $\sigma_0 := \frac{1}{3}\boldsymbol{\sigma}:\mathbf{I}$, and deviatoric part, $\mathbf{S} = dev\boldsymbol{\sigma}$, $\boldsymbol{\sigma} = \sigma_0\mathbf{I} + \mathbf{S}$, we elaborate Eq.(115)

$$\begin{aligned} \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1} \cdot \frac{d\mathbf{U}_t(\eta)}{d\eta} = \sigma_0 \ln \left(\frac{J_t(1)}{J_t(0)} \right) \frac{d\varphi_v}{d\eta} + \sigma_0 \mathbf{I} : \left\{ \ln(\mathbf{B}_\varepsilon) \frac{d\bar{\phi}}{d\eta} \right\} + \\ \mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : \left\{ \mathbf{H}_{dd}(1) \circ \frac{d\boldsymbol{\varphi}_{dd}}{d\eta} + \mathbf{H}_{of}(1) \circ \frac{d\boldsymbol{\varphi}_{of}}{d\eta} + dev \ln(\mathbf{B}_\varepsilon) \frac{d\bar{\phi}}{d\eta} \right\}. \end{aligned} \quad (116)$$

Thus, for $diag[\ln(\mathbf{B}_\varepsilon)] = 0$, the mean Cauchy stress contributes to the driving force X through the volumetric transformation work $\sigma_0 \ln(J_t(1)/J_t(0))$ only, and the deviatoric Cauchy stress contributes to the driving force X through the corresponding transformation work as well, both as desired. This is the main advantage of the Eqs.(100)-(108). By adding a spherical part to $\ln(\mathbf{B}_\varepsilon)$, one can get extra contribution to the volumetric transformation unrelated to the transformation strains at $\eta = 0$ and $\eta = 1$. The off-diagonal part of $\ln(\mathbf{B}_\varepsilon)$ allows one to take into account into X the contribution of the stresses, for which conjugate components of the transformation strain are lacking.

Similarly, we evaluate the stress contribution to the instability criterion Eq.(27)

$$\begin{aligned}
 & \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \mathbf{U}_t^{-1} \cdot \frac{d^2 \mathbf{U}_t(\hat{\eta})}{d\eta^2} = \\
 & \mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} : \left\{ H_v(1) \mathbf{I} \frac{d^2 \boldsymbol{\varphi}_v(\hat{\eta})}{d\eta^2} + \mathbf{H}_{dd}(1) \circ \frac{d^2 \boldsymbol{\varphi}_{dd}(\hat{\eta})}{d\eta^2} + \mathbf{H}_{of}(1) \circ \frac{d^2 \boldsymbol{\varphi}_{of}(\hat{\eta})}{d\eta^2} + \ln(\mathbf{B}_\varepsilon) \frac{d^2 \bar{\phi}(\hat{\eta})}{d\eta^2} \right\} = \\
 & \sigma_0 \ln \left(\frac{J_t(1)}{J_t(0)} \right) \frac{d^2 \varphi_v(\hat{\eta})}{d\eta^2} + \sigma_0 \mathbf{I} : \left\{ \ln(\mathbf{B}_\varepsilon) \frac{d^2 \bar{\phi}(\hat{\eta})}{d\eta^2} \right\} + \\
 & \mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : \left\{ \mathbf{H}_{dd}(1) \circ \frac{d^2 \boldsymbol{\varphi}_{dd}(\hat{\eta})}{d\eta^2} + \mathbf{H}_{of}(1) \circ \frac{d^2 \boldsymbol{\varphi}_{of}(\hat{\eta})}{d\eta^2} + dev \ln(\mathbf{B}_\varepsilon) \frac{d^2 \bar{\phi}(\hat{\eta})}{d\eta^2} \right\}. \quad (117)
 \end{aligned}$$

This expression has the same advantages as the expression for the driving force X . Namely, for $diag[\ln(\mathbf{B}_\varepsilon)] = 0$, σ_0 participates in the instability criterion through the volumetric transformation work $\sigma_0 \ln(J_t(1)/J_t(0))$ only, and \mathbf{S} participates through the corresponding transformation work as well, both as desired. By adding a spherical part to $\ln(\mathbf{B}_\varepsilon)$, one can get extra contribution of σ_0 to the instability condition. The off-diagonal part of $\ln(\mathbf{B}_\varepsilon)$ allows one to include the effect on the lattice instability condition of the stresses for which corresponding components of the transformation strain are absent.

8.6. Elastic energy

The general expression for elastic energy is

$$\psi^e(\mathbf{E}_e, \theta, \mathbf{C}^k(\eta)) = \frac{1}{2} \mathbf{E}_e : \mathbf{C}(\eta) : \mathbf{E}_e + \frac{1}{3!} (\mathbf{E}_e : \mathbf{C}^3(\eta) : \mathbf{E}_e) : \mathbf{E}_e + \frac{1}{4!} \mathbf{E}_e : (\mathbf{E}_e : \mathbf{C}^4(\eta) : \mathbf{E}_e) : \mathbf{E}_e + \dots \quad (118)$$

with elastic moduli of the k^{th} rank

$$\begin{aligned}
 \mathbf{C}(\eta) &= \mathbf{C}_0 + (\mathbf{C}_1 - \mathbf{C}_0) \varphi(a_{c2}, w_{c2}, \eta); \\
 \mathbf{C}^3(\eta) &= \mathbf{C}_0^3 + (\mathbf{C}_1^3 - \mathbf{C}_0^3) \varphi(a_{c3}, w_{c3}, \eta); \\
 \mathbf{C}^4(\eta) &= \mathbf{C}_0^4 + (\mathbf{C}_1^4 - \mathbf{C}_0^4) \varphi(a_{c4}, w_{c4}, \eta). \quad (119)
 \end{aligned}$$

Similar to the second-rank transformation strain tensor each component of the k^{th} rank elastic moduli tensor can be multiplied by function $\varphi(a_{ck}, w_{ck}, \eta)$ with different scalars a_{ck} and w_{ck} .

8.7. Lattice instability criteria for chosen interpolation functions

For transformation strain $\boldsymbol{\varepsilon}_t$ related interpolation. Substituting in the general lattice instability criterion (27) all specific functions, namely elastic constants (118) and (119) with interpolation function (35) and Eqs. (72), (73), and (76) for other interpolating functions, as well as Eqs. (87) and (88) one obtains more explicit criteria for the direct and reverse PTs:

$$\begin{aligned} P_0 \rightarrow P_1 : \quad \rho \frac{\partial X}{\partial \eta} &= (\mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} - \frac{\psi^e}{J_e} \mathbf{I}) : 2 (\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{a}_\varepsilon + \mathbf{A}_\varepsilon) \\ &- \frac{2}{J_e} \left[\frac{a_{c2}}{2} \mathbf{E}_e : (\mathbf{C}_1 - \mathbf{C}_0) : \mathbf{E}_e + \frac{a_{c3}}{3!} (\mathbf{E}_e : (\mathbf{C}_1^3 - \mathbf{C}_0^3) : \mathbf{E}_e) : \mathbf{E}_e + \frac{a_{c4}}{4!} \mathbf{E}_e : (\mathbf{E}_e : (\mathbf{C}_1^4 - \mathbf{C}_0^4) : \mathbf{E}_e) : \mathbf{E}_e \right] \\ &- 2\rho_0 [(A(\theta) + (a-3)\Delta\psi^\theta(\theta))] - \frac{6\rho_0}{J_e} \Delta\psi^\theta(\theta) \geq 0; \end{aligned} \quad (120)$$

$$\begin{aligned} P_1 \rightarrow P_0 : \quad \rho \frac{\partial X}{\partial \eta} &= (\mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} - \frac{\psi^e}{J_e} \mathbf{I}) : \mathbf{U}_t^{-1}(1) \cdot 2 [\Delta \boldsymbol{\varepsilon}_t \circ \mathbf{w}_\varepsilon + \mathbf{A}_\varepsilon] \\ &- \frac{2}{J_e} \left[\frac{w_{c2}}{2} \mathbf{E}_e : (\mathbf{C}_1 - \mathbf{C}_0) : \mathbf{E}_e + \frac{w_{c3}}{3!} (\mathbf{E}_e : (\mathbf{C}_1^3 - \mathbf{C}_0^3) : \mathbf{E}_e) : \mathbf{E}_e + \frac{a_{w4}}{4!} \mathbf{E}_e : (\mathbf{E}_e : (\mathbf{C}_1^4 - \mathbf{C}_0^4) : \mathbf{E}_e) : \mathbf{E}_e \right] - \\ &2\rho_0 [(A(\theta) + (a-3)\Delta\psi^\theta(\theta))] + \frac{6\rho_0}{J} \Delta\psi^\theta(\theta) \geq 0, \quad \eta = \hat{\eta}. \end{aligned} \quad (121)$$

For interpolation of the logarithmic transformation strain $\ln \mathbf{U}_t$ that separates volumetric and deviatoric parts. Instead of expression (76) for $\boldsymbol{\varepsilon}_t(\eta)$ we will use Eqs.(100)-(108) utilizing separate interpolation functions for spherical and components of deviatoric logarithmic transformation strain, as well as Eqs.(114) and (117) for the second derivative of \mathbf{U}_t and corresponding stress work. Thus, we obtain

$$\begin{aligned} P_0 \rightarrow P_1 : \quad \rho \frac{\partial X}{\partial \eta} &= 2(\sigma_0 - \frac{\psi^e}{J_e}) \ln \left(\frac{J_t(1)}{J_t(0)} \right) a_v + 2(\sigma_0 - \frac{\psi^e}{J_e}) \mathbf{I} : \ln(\mathbf{B}_\varepsilon) + \\ &2\mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : \{ \mathbf{H}_{dd}(1) \circ \mathbf{a}_{dd} + \mathbf{H}_{of}(1) \circ \mathbf{a}_{of} + dev \ln(\mathbf{B}_\varepsilon) \} \\ &- \frac{2}{J_e} \left[\frac{a_{c2}}{2} \mathbf{E}_e : (\mathbf{C}_1 - \mathbf{C}_0) : \mathbf{E}_e + \frac{a_{c3}}{3!} (\mathbf{E}_e : (\mathbf{C}_1^3 - \mathbf{C}_0^3) : \mathbf{E}_e) : \mathbf{E}_e + \frac{a_{c4}}{4!} \mathbf{E}_e : (\mathbf{E}_e : (\mathbf{C}_1^4 - \mathbf{C}_0^4) : \mathbf{E}_e) : \mathbf{E}_e \right] \\ &- 2\rho_0 [(A(\theta) + (a-3)\Delta\psi^\theta(\theta))] - \frac{6\rho_0}{J_e} \Delta\psi^\theta(\theta) \geq 0; \end{aligned} \quad (122)$$

$$\begin{aligned}
 P_1 \rightarrow P_0 : \quad & \rho \frac{\partial X}{\partial \eta} = 2(\sigma_0 - \frac{\psi^e}{J_e}) \ln \left(\frac{J_t(1)}{J_t(0)} \right) w_v + 2(\sigma_0 - \frac{\psi^e}{J_e}) \mathbf{I} : \ln(\mathbf{B}_\varepsilon) + \\
 & 2\mathbf{F}_e^t \cdot \mathbf{S} \cdot \mathbf{F}_e^{t-1} : \{ \mathbf{H}_{dd}(1) \circ \mathbf{w}_{dd} + \mathbf{H}_{of}(1) \circ \mathbf{w}_{of} + dev \ln(\mathbf{B}_\varepsilon) \} \\
 & - \frac{2}{J_e} \left[\frac{w_{c2}}{2} \mathbf{E}_e : (\mathbf{C}_1 - \mathbf{C}_0) : \mathbf{E}_e + \frac{w_{c3}}{3!} (\mathbf{E}_e : (\mathbf{C}_1^3 - \mathbf{C}_0^3) : \mathbf{E}_e) : \mathbf{E}_e + \frac{a_{w4}}{4!} \mathbf{E}_e : (\mathbf{E}_e : (\mathbf{C}_1^4 - \mathbf{C}_0^4) : \mathbf{E}_e) : \mathbf{E}_e \right] - \\
 & 2\rho_0 [(A(\theta) + (a-3)\Delta\psi^\theta(\theta)] + \frac{6\rho_0}{J} \Delta\psi^\theta(\theta) \geq 0, \quad \eta = \hat{\eta}.
 \end{aligned} \tag{123}$$

9. Specification for Si I ↔ Si II phase transformations

9.1. Transformation strains

Instability conditions for cubic to tetragonal PTs Si I ↔ Si II were obtained with the help of MD simulations for various combinations of all six components of the Cauchy stress tensor in Levitas et al. (2017a,b). We accept $\mathbf{U}_t(0) = \mathbf{I}$ for the cubic state and skip (1) for the product tetragonal state. In the cubic axes, components $\varepsilon_{t1} = \varepsilon_{t2} = 0.1753$ and $H_1 = \ln U_{t1} = \ln U_{t2} = 0.1615$ (extension); $\varepsilon_{t3} = -0.447$ and $H_3 = \ln U_{t3} = -0.5924$ (compression), i.e., $J_t = (1 + \varepsilon_{t1})^2(1 + \varepsilon_{t3}) = 0.764$ and $tr\mathbf{H} = \ln J_t = -0.2694$. Components of $\mathbf{H}_{dd}(1) = dev\mathbf{H}$ are $H_{d1} = H_{d2} = 0.2513$ and $H_{d3} = -2H_{d1} = -0.5026$. Then for the reverse PT $\mathbf{U}_t^r = \mathbf{U}_t^{-1}$ with components $\varepsilon_{t1}^r = \varepsilon_{t2}^r = -0.1492$ and $\ln U_{t1}^r = \ln U_{t2}^r = -0.1615$; $\varepsilon_{t3}^r = 0.8083$ and $\ln U_{t3}^r = 0.5924$. Instability conditions have been described in terms of normal stresses σ_i along the cubic axes; the effect of shear stresses was negligible and we will not consider it. This in particular means that the tensors \mathbf{A}_ε and $\ln\mathbf{B}_\varepsilon$, which describe the effect of the off-diagonal components of the Cauchy stress, are negligible as well, $\mathbf{A}_\varepsilon = \ln\mathbf{B}_\varepsilon = 0$.

9.2. Lattice instability conditions from MD simulations

For the loading by three stresses normal to the cubic faces, tensors $\boldsymbol{\sigma}$, \mathbf{F}_e , \mathbf{U}_t , their inverse and η -derivatives are coaxial and can be permuted in the scalar product. Thus, $\mathbf{F}_e^t \cdot \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} = \boldsymbol{\sigma} \cdot \mathbf{F}_e^{t-1} \cdot \mathbf{F}_e^t = \boldsymbol{\sigma}$.

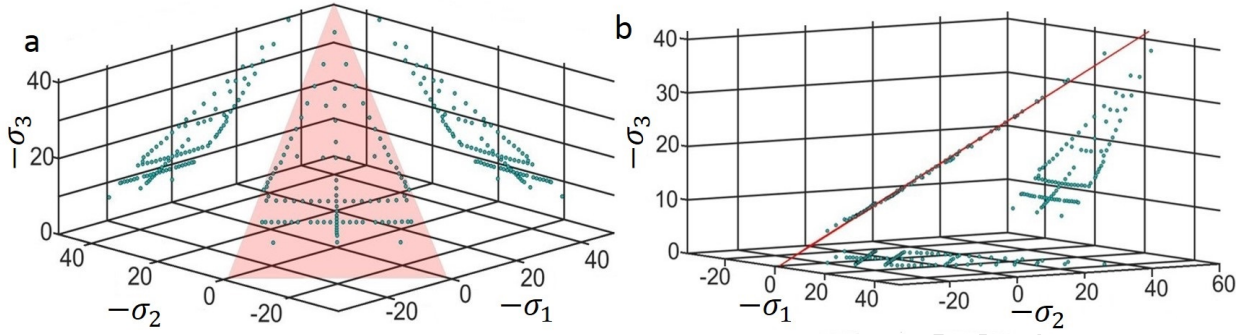


Figure 4: Confirmation of crystal lattice instability criterion (124) for direct Si I→Si II PT. (A) Plane in stress space σ_i corresponding to the instability criterion (124) and instability points from MD simulations. Projections of each point on $\sigma_i - \sigma_j$ planes allow one to determine coordinates of each point in stress space. (B) The same plot as in (A) but rotated until theoretical plane (124) is visible as a line, to demonstrate how close all simulation points are to the theoretical plane. Adopted from Levitas et al. (2017b).

Lattice instability conditions at 1 K obtained with the help of atomistic simulations are approximated in Levitas et al. (2017a) as

$$P_0 \rightarrow P_1 : \quad 0.361195(\sigma_1 + \sigma_2) - \sigma_3 \geq 12.2978 \text{ GPa} \text{ for } \sigma_3 > -6.23782 \text{ GPa} \quad (124)$$

$$P_1 \rightarrow P_0 : \quad 0.19200(\sigma_1 + \sigma_2) - \sigma_3 \leq 9.45916 \text{ GPa}, \quad (125)$$

see Figs. 4 and 5. Under hydrostatic loading, instability stress $\sigma_1 = \sigma_2 = \sigma_3 = -46.75 \text{ GPa}$ for the direct PT and -15.36 GPa for the reverse PT.

Intersection of the instability planes (124) and (125) in stress space corresponds to $\sigma_3 = -6.23782 \text{ GPa}$ and $\sigma_1 + \sigma_2 = -16.7775 \text{ GPa}$. While for reverse PT plane (125) describes instability in the whole stress ranges, for direct PT for $\sigma_3 < -6.23782 \text{ GPa}$ (or equivalently, $\sigma_1 + \sigma_2 < -16.7775 \text{ GPa}$), there is a jump from the plane (124) to (125), i.e, instability criteria for direct and reverse PTs coincide (Fig. 5):

$$P_0 \rightarrow P_1 : \quad 0.19200(\sigma_1 + \sigma_2) - \sigma_3 \leq 9.45916 \text{ GPa} \text{ for } \sigma_3 < -6.23782 \text{ GPa}. \quad (126)$$

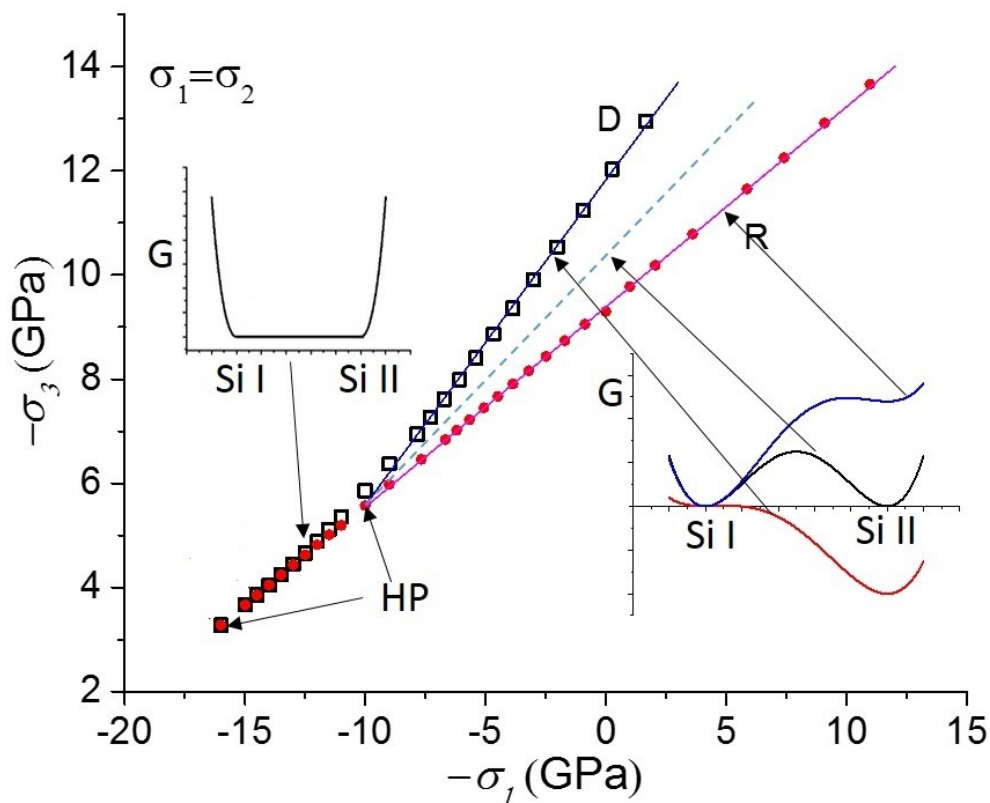


Figure 5: Relationships between stresses σ_3 and $\sigma_1 = \sigma_2$ for crystal lattice instability for direct and reverse Si I \leftrightarrow Si II PTs. Each instability line corresponds to the disappearance of the minimum in the Gibbs energy G plot for the corresponding phase. The dashed line is the schematic phase equilibrium line determined by the equality of the Gibbs energy of phases. When two instability lines merge, Gibbs energy has a plateau with a constant value leading to an unique homogeneous and hysteresis-free first-order Si I \leftrightarrow Si II PT, with a continuum of intermediate homogeneous phases (HP), which are in indifferent thermodynamic equilibrium. Adopted from Levitas et al. (2017a).

Note that qualitatively most of the MD results obtained in Levitas et al. (2017a,b) can be described with the simplest geometrically nonlinear elastic model (Levitas (2017)).

9.3. Interpolation functions for the elastic moduli and the modified transformation work instability criteria

Elastic moduli. Since instability conditions are linear in stresses, all nonlinear-in-stresses terms in Eqs.(120) and (121) should be either identically equal to zero or nonlinearity should be negligible. According to atomistic simulations in Levitas et al. (2017a,b), the jump in elastic energy is large. Thus, to eliminate corresponding nonlinearity, it is reasonable to assume that the second derivatives of the corresponding approximating functions are zero for $\eta = 0$ and 1, i.e., according to Eqs.(42)

$$\varphi(a_{c2}, w_{c2}, \eta) = \varphi(a_{c3}, w_{c3}, \eta) = \varphi(a_{c4}, w_{c3}, \eta) = \varphi(0, 0, \eta) = \eta^3(10 - 15\eta + 6\eta^2). \quad (127)$$

Thus, Eqs.(120) and (121) simplify to

$$P_0 \rightarrow P_1 : \quad (\boldsymbol{\sigma} - \frac{\psi^e}{J_e} \mathbf{I}) : \boldsymbol{\varepsilon}_t \circ \mathbf{a}_\varepsilon - \rho_0 [(A(\theta) + (a - 3)\Delta \psi^\theta(\theta)] - \frac{3\rho_0}{J_e} \Delta \psi^\theta(\theta) \geq 0 \quad (128)$$

$$P_1 \rightarrow P_0 : \quad (\boldsymbol{\sigma} - \frac{\psi^e}{J_e} \mathbf{I}) : \mathbf{U}_t^{-1}(1) \cdot \boldsymbol{\varepsilon}_t \circ \mathbf{w}_\varepsilon - \rho_0 [(A(\theta) + (a - 3)\Delta \psi^\theta(\theta)] + \frac{3\rho_0}{J} \Delta \psi^\theta(\theta) \geq 0 \quad (129)$$

and Eqs.(122) and (123) simplify to

$$\begin{aligned} P_0 \rightarrow P_1 : \quad & (\sigma_0 - \frac{\psi^e}{J_e}) \ln(J_t(1)) a_v + \mathbf{S} : \{\mathbf{H}_{dd}(1) \circ \mathbf{a}_{dd}\} \\ & - \rho_0 [(A(\theta) + (a - 3)\Delta \psi^\theta(\theta)] - \frac{3\rho_0}{J_e} \Delta \psi^\theta(\theta) \geq 0; \end{aligned} \quad (130)$$

$$\begin{aligned} P_1 \rightarrow P_0 : \quad & (\sigma_0 - \frac{\psi^e}{J_e}) \ln(J_t(1)) w_v + \mathbf{S} : \{\mathbf{H}_{dd}(1) \circ \mathbf{w}_{dd}\} \\ & - \rho_0 [(A(\theta) + (a - 3)\Delta \psi^\theta(\theta)] + \frac{3\rho_0}{J} \Delta \psi^\theta(\theta) \geq 0. \end{aligned} \quad (131)$$

Cubic to tetragonal PT. Elaborating the first term in Eqs.(128) and (129) for cubic to tetragonal PT, we obtain

$$\begin{aligned} P_0 \rightarrow P_1 : \quad W_d := & (\sigma_1 + \sigma_2)\varepsilon_{t1}a_{\varepsilon 1} + \sigma_3\varepsilon_{t3}a_{\varepsilon 3} \geq \\ & -\frac{\psi^e}{J_e}(2\varepsilon_{t1}a_{\varepsilon 1} + \varepsilon_{t3}a_{\varepsilon 3}) + \rho_0 [A(\theta) + (a-3)\Delta\psi^\theta(\theta)] + \frac{3\rho_0}{J_e}\Delta\psi^\theta(\theta); \end{aligned} \quad (132)$$

$$\begin{aligned} P_1 \rightarrow P_0 : \quad W_r := & (\sigma_1 + \sigma_2)\frac{\varepsilon_{t1}w_{\varepsilon 1}}{1 + \varepsilon_{t1}} + \frac{\sigma_3\varepsilon_{t3}w_{\varepsilon 3}}{1 + \varepsilon_{t3}} \geq \\ & -\frac{\psi^e}{J_e}\left(\frac{2\varepsilon_{t1}w_{\varepsilon 1}}{1 + \varepsilon_{t1}} + \frac{\varepsilon_{t3}w_{\varepsilon 3}}{1 + \varepsilon_{t3}}\right) + \rho_0 [A(\theta) + (a-3)\Delta\psi^\theta(\theta)] - \frac{3\rho_0}{J}\Delta\psi^\theta(\theta), \end{aligned} \quad (133)$$

where W represents a modified transformation work, which for $a_{\varepsilon 1} = a_{\varepsilon 3} = -w_{\varepsilon 1} = -w_{\varepsilon 3}$ reduces to the traditional transformations work.

For Eqs.(130) and (131), let us first specify the terms proportional to \mathbf{S} while taking into account constraints (104). Due to $H_{dd}^{11}(1) = H_{dd}^{22}(1)$, $a_d^{11} = a_d^{22}$, and $w_d^{11} = w_d^{22}$, the constraints (104) simplify to

$$a_d^{11} = a_d^{22} = a_d^{33} = a_d; \quad w_d^{11} = w_d^{22} = w_d^{33} = w_d, \quad (134)$$

i.e., all components of the deviatoric strain for the cubic to tetragonal transformation have the same interpolation functions. Then with allowing for $H_{dd}^3(1) = -2H_{dd}^{11}(1)$ and $S_3 = -(S_1 + S_2)$, one obtains

$$\begin{aligned} \mathbf{S} : \{\mathbf{H}_{dd}(1) \circ \mathbf{a}_{dd}\} &= \mathbf{S} : \mathbf{H}_{dd}(1)a_d = 3S_3H_{dd}^{33}(1)a_d/2 = (2\sigma_3 - \sigma_1 - \sigma_2)H_{dd}^{33}(1)a_d/2; \\ \mathbf{S} : \{\mathbf{H}_{dd}(1) \circ \mathbf{w}_{dd}\} &= \mathbf{S} : \mathbf{H}_{dd}(1)w_d = 3S_3H_{dd}^{33}(1)w_d/2 = (2\sigma_3 - \sigma_1 - \sigma_2)H_{dd}^{33}(1)w_d/2. \end{aligned} \quad (135)$$

Then Eqs.(130) and (131) specify to

$$\begin{aligned} P_0 \rightarrow P_1 : \quad & (\sigma_0 - \frac{\psi^e}{J_e}) \ln(J_t(1)) a_v + (2\sigma_3 - \sigma_1 - \sigma_2)H_{dd}^{33}(1)a_d/2 \\ & -\rho_0 [A(\theta) + (a-3)\Delta\psi^\theta(\theta)] - \frac{3\rho_0}{J_e}\Delta\psi^\theta(\theta) \geq 0; \end{aligned} \quad (136)$$

$$\begin{aligned}
 P_1 \rightarrow P_0 : \quad & (\sigma_0 - \frac{\psi^e}{J_e}) \ln(J_t(1)) w_v + (2\sigma_3 - \sigma_1 - \sigma_2) H_{dd}^{33}(1) w_d / 2 \\
 & - \rho_0 [A(\theta) + (a - 3) \Delta \psi^\theta(\theta)] + \frac{3\rho_0}{J} \Delta \psi^\theta(\theta) \geq 0.
 \end{aligned} \tag{137}$$

9.4. Specification of lattice instability conditions

The term $\rho_0 \Delta \psi^\theta(\theta)$ can be estimated from the thermodynamic equilibrium equation under hydrostatic condition. Thus, neglecting elastic strain and change in elastic moduli during PT, we obtain $\sigma_0^{eq}(J_t - 1) = \rho_0 \Delta \psi^\theta(\theta)$. Under quasi-hydrostatic conditions, phase equilibrium mean stress σ_0^{eq} for PTs Si I \leftrightarrow Si II at room temperature is -10.5 GPa (Voronin et al. (2003)). At 1 K, it should be between instability mean stresses -15.36 and -46.75 GPa . For the best approximation of the stress-strain curve for the hydrostatic loading in Part II of this paper (Levitas (2018)), we accept $\sigma_0^{eq} = -26.9 \text{ GPa}$ and get $\rho_0 \Delta \psi^\theta = 6.35 \text{ GPa}$ for the transformation strain based kinematic model. Besides, we accept $\sigma_0^{eq} = -27.20 \text{ GPa}$ and get $\rho_0 \Delta \psi^\theta = 6.42 \text{ GPa}$ for the logarithmic strain based model.

Substituting all numerical values of material parameters in Eqs.(132) and (133) as well as Eqs.(136) and (137) we specify the instability criteria for the transformation strain based model:

$$\begin{aligned}
 P_0 \rightarrow P_1 : \quad & W_d := 0.39217(\sigma_1 + \sigma_2) \frac{a_{\varepsilon 1}}{a_{\varepsilon 3}} - \sigma_3 \geq \\
 & - \frac{\psi^e}{J_e} \left(0.78434 \frac{a_{\varepsilon 1}}{a_{\varepsilon 3}} - 1 \right) + \frac{2.2371 \rho_0 A(\theta)}{a_{\varepsilon 3}} + \frac{14.2058a}{a_{\varepsilon 3}} + \frac{42.6174}{a_{\varepsilon 3}} \left(\frac{1}{J_e} - 1 \right); \tag{138}
 \end{aligned}$$

$$\begin{aligned}
 P_1 \rightarrow P_0 : \quad & W_r := 0.184523(\sigma_1 + \sigma_2) \frac{w_{\varepsilon 1}}{w_{\varepsilon 3}} - \sigma_3 \leq \\
 & - \frac{\psi^e}{J_e} \left(0.369046 \frac{w_{\varepsilon 1}}{w_{\varepsilon 3}} - 1 \right) + \frac{1.2371 \rho_0 A(\theta)}{w_{\varepsilon 3}} + \frac{7.8558a}{w_{\varepsilon 3}} - \frac{23.5674}{w_{\varepsilon 3}} \left(\frac{1}{J} + 1 \right), \tag{139}
 \end{aligned}$$

and for the logarithmic strain based model:

$$\begin{aligned}
 P_0 \rightarrow P_1 : \quad & W_d := (\sigma_1 + \sigma_2) \frac{0.2513 - 0.0898a_v/a_d}{0.5026 + 0.0898a_v/a_d} - \sigma_3 \geq \\
 & \frac{\rho_0 A(\theta)/a_d - 4.72(3 - a - 3/J_e)/a_d - (a_v/a_d)(0.26935\psi^e)/J_e}{0.5026 + 0.0898a_v/a_d}; \tag{140}
 \end{aligned}$$

$$P_1 \rightarrow P_0 : \quad W_r := (\sigma_1 + \sigma_2) \frac{0.2513 - 0.0898w_v/w_d}{0.5026 + 0.0898w_v/w_d} - \sigma_3 \leq \frac{\rho_0 A(\theta)/w_d - 6.35(3 - a + 3/J)/w_d - (w_v/w_d)(0.26935\psi^e)/J_e}{0.5026 + 0.0898w_v/w_d}, \quad (141)$$

where the sign of the inequality in Eqs.(139) and (141) is changed because $w_{\varepsilon 3} < 0$ and $0.5026w_d + 0.0898w_v < 0$. Comparing Eqs.(138)-(139) and Eqs.(140)-(141) with corresponding instability criteria for Si I \leftrightarrow Si II PT in Eqs. (124) and (125) we obtain that

$$\frac{a_{\varepsilon 1}}{a_{\varepsilon 3}} = 0.9210; \quad 0.3848 \frac{\psi^e}{J_e} + \frac{2.2371\rho_0 A(\theta)}{a_{\varepsilon 3}} + \frac{14.2058a}{a_{\varepsilon 3}} + \frac{42.6174}{a_{\varepsilon 3}} \left(\frac{1}{J_e} - 1 \right) = 12.2978; \quad (142)$$

$$\frac{w_{\varepsilon 1}}{w_{\varepsilon 3}} = 1.0405; \quad 0.6160 \frac{\psi^e}{J_e} + \frac{1.2371\rho_0 A(\theta)}{w_{\varepsilon 3}} + \frac{7.8558a}{w_{\varepsilon 3}} - \frac{23.5674}{w_{\varepsilon 3}} \left(\frac{1}{J} + 1 \right) = 9.4592. \quad (143)$$

$$\frac{a_v}{a_d} = 0.5707; \quad -0.1537 \frac{\psi^e}{J_e} + \frac{\rho_0 A(\theta)}{a_d} + \frac{6.42a}{a_d} + \frac{19.26}{a_d} \left(\frac{1}{J_e} - 1 \right) = 6.8112; \quad (144)$$

$$\frac{w_v}{w_d} = 1.4462; \quad -0.389527 \frac{\psi^e}{J_e} + \frac{\rho_0 A(\theta)}{w_d} + \frac{6.42a}{w_d} - \frac{19.26}{w_d} \left(\frac{1}{J} + 1 \right) = 5.98263. \quad (145)$$

Since nonlinear-in-stress terms ψ^e , J_e , and J should not visibly contribute to the instability criteria, their effect should be insignificant. Usually, elastic energy is an order of magnitude smaller than stresses and terms with ψ^e could be neglected from the very beginning. In MD simulations the elastic strain of Si II is much smaller than the transformation strain, so we assume $J \simeq J_t = 0.7639$. In contrast elastic strain of Si I was relatively large and we assume $J_e = 0.95$.

Material parameters for transformation strain based interpolation functions. Then Eqs. (142) and (143) simplify

$$2.2371\rho_0 A(\theta) + 14.2058a + 2.2430 = 12.2978a_{\varepsilon 3}; \quad (146)$$

$$1.2371\rho_0 A(\theta) + 7.8558a - 54.4147 = 9.4592w_{\varepsilon 3}. \quad (147)$$

Since A and a contribute in the same proportion to both equations, they can be excluded:

$$w_{\varepsilon 3} = -5.8837 + 0.7189a_{\varepsilon 3}; \quad 0 \leq a_{\varepsilon 3} \leq 8.1843. \quad (148)$$

Condition $a_{\varepsilon 3} \leq 8.1843$ follows from $w_{\varepsilon 3} \leq 0$. Since there is some freedom in choosing a_3 and $w_{\varepsilon 3}$ we can impose an additional condition that $w_{\varepsilon 3} = a_{\varepsilon 3} - 6$, which is required for disappearance of the term with η^5 . Then we obtain

$$a_{\varepsilon 3} = 0.4138; \quad w_{\varepsilon 3} = -5.5862; \quad a_{\varepsilon 1} = 0.3811; \quad w_{\varepsilon 1} = -5.8124. \quad (149)$$

Substituting $a_{\varepsilon 3}$ in Eq.(146) (or $w_{\varepsilon 3}$ in Eq.(147)), since these equations are linearly dependent), one obtains

$$\rho_0 A(\theta) + 6.35a = 1.2721. \quad (150)$$

Since both A and a contribute to the thermal free energy (72) in the same combination as in Eq.(150), there is no way to separately determine A and a , and this is not necessary.

Note that for any $0 \leq a_{\varepsilon 3} \leq 8.1843$ the plots of the functions $\varepsilon_{t1}(\eta)$ and $\varepsilon_{t3}(\eta)$ are visually undistinguishable, while they have slightly different second derivatives at $\eta = 0$ and 1. This is not surprising. For example, for the fourth-degree polynomial (Fig. 1(b)), when a varies from 0 to 6, the polynomial does not change significantly visually but the second derivatives at $\eta = 0$ and 1 change drastically, and corresponding instability stress tends to infinity for $a = 0$ for direct PT and for $a = 6$ for the reverse PT.

Material parameters for logarithmic transformation strain based interpolation functions. Similarly, Eqs. (144) and (145) simplify to

$$\rho_0 A(\theta) + 6.42a + 1.0136 = 6.8112a_d; \quad (151)$$

$$\rho_0 A(\theta) + 6.42a - 44.4727 = 5.98263w_d, \quad (152)$$

which results in

$$w_d = -7.6031 + 1.1385a_d; \quad 0 \leq a_d \leq 6.6781. \quad (153)$$

Condition $a_d \leq 6.6781$ follows from $w_d \leq 0$. Since there is some freedom in choosing a_d , we can impose an additional condition that the magnitude of the second derivatives at $\eta = 0$ and 1 is the same, i.e. $w_d = -a_d$. Then we obtain

$$w_d = -a_d = -3.5553; \quad a_v = 2.0290; \quad w_v = -5.1416. \quad (154)$$

Substituting a_d in Eq.(151) (or w_d in Eq.(152), since these equations are linearly dependent), one obtains

$$\rho_0 A(\theta) + 2.481a = 23.2022. \quad (155)$$

10. Concluding remarks

After formulating the general structure of the PFA equations coupled to mechanics, the main problem is in formulating the local thermodynamic potential, namely in the interpolation of all material properties between different phases and introducing proper energetic barriers between them. The initial requirements for energy were that it has as many local minima as there are phases one considers and that it is invariant with respect to an exchange of any symmetry-related martensitic variants. More advanced theories imposed conditions on the interpolation and barrier functions, which specify the values of the order parameter(s) and zero first derivatives for each equilibrium phase. These conditions could be met within the fourth-degree interpolating polynomials.

In this paper, we utilized the crystal lattice instability conditions for PTs Si I \leftrightarrow Si II under multiaxial loading obtained with MD simulations in Levitas et al. (2017a,b) in order to essentially advance PFA for stress-induced martensitic or reconstructive PTs. MD results in

Levitas et al. (2017a,b) are (to our best knowledge) the first instability conditions obtained under action of all six components of the stress tensor. Accordingly, our current paper is the first one which utilizes such information for formulating new requirements to the thermodynamic potential and transformation strain tensor and developing new PFA that satisfies these requirements. This was done for the general large strain formulation with higher order nonlinear elastic energy, and with allowing for interfacial stresses. The crystal lattice instability criteria are derived for such a general case and it is proven that they are independent of the prescribed stress measure. In order to reproduce the lattice instability conditions obtained with MD:

- (a) one has to use the fifth degree polynomial interpolation functions of η for all material parameters;
- (b) each independent component of the transformation strain tensor should have different interpolation functions;
- (c) interpolation functions for tensors of the elastic moduli of all ranks should have zero second derivatives for the parent and product phases, so that the elastic energy (which is nonlinear in stresses) does not contribute to the lattice instability conditions.

Specific interpolation and double-well functions have been derived for all parts of the Helmholtz free energy as well as for two models for the transformation deformation gradient: based on interpolation of the transformation strain and logarithmic transformation strain. For these models explicit expressions for the thermodynamic driving force in the Ginzburg-Landau equation and the lattice instability conditions are derived. Material parameters have been calibrated for both kinematic models using results of MD simulations.

In Part II of this paper (Levitas (2018)), the developed model is further refined and studied, and applied for the finite element simulations of the nanostructure evolution in Si under triaxial loading. A developed theory can be generalized for twinning, dislocations, multiple martensitic variants, and multiphase systems. Similar instability conditions can be

determined under action of multiaxial electromagnetic fields.

Developed quantitative PFA will allow one to develop a quantitative theory for barrierless nucleation at various types of defects, like dislocations, grain and twin boundaries, and external surface. Even for steels there is no quantitative PFA to martensite nucleation, see Olson and Cohen (1972, 1986); Olson and Roytburd (1995). Stability of the propagating interfaces can be studied using methods developed in Grinfeld (1991). In order to explain the drastic reduction, by an order of magnitude, of the PT pressure by superposed plastic deformations (Ji et al. (2012); Levitas and Shvedov (2002)), the nucleation at the dislocation pile up is modeled analytically (Levitas (2004,a)) and with PFA in Javanbakht and Levitas (2015, 2016); Levitas and Javanbakht (2014, 2015). However, all of the above studies were performed for a model materials. The current model allows quantitative studies for Si.

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- New requirements for the thermodynamic potential, which allow one to satisfy the lattice instability conditions are formulated.
- Phase field approach that satisfies these requirements and includes interfacial stresses and large strains is developed.
- It is proved that the lattice instability criteria are independent of the type of the prescribed stress tensor.
- Fifth degree polynomial interpolation functions of the order parameter have to be used.
- Different components of the transformation strain should have different interpolation functions.