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Three-dimensional Landau theory for multivariant stress-induced martensitic phase transformations. III. Alternative potentials, critical nuclei, kink solutions, and dislocation theory

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In part III of this paper, alternative Landau potentials for the description of stress-and temperature-induced martensitic phase transformations under arbitrary three-dimensional loading are obtained. These alternative potentials include a sixth-degree (2-4-6) polynomial in Cartesian order parameters and a potential in hyperspherical order parameters. Each satisfies all conditions for the correct description of experiments. The unique features of the potentials are pointed out and a detailed comparison of the potentials is made for NiAl alloy. Analytic solutions of the one-dimensional time-independent Ginzburg-Landau equations for the 2-3-4 and 2-4-6 potentials for a constant-stress tensor and invariant-plane strain are obtained and compared. Solutions include martensitic and austenitic critical nuclei and diffuse martensite-austenite and martensite-martensite interfaces. The widths and energies of the nuclei and interfaces are functions of the thermodynamic driving force, the gradient energy coefficient, and a parameter that characterizes the stability of austenite. The splitting of a martensite-martensite interface into two austenite-martensite interfaces is interpreted as a potentially new mechanism—namely, barrierless austenite nucleation—which might be observed experimentally at the interface between two invariant-plane-strain variants. The widths, energies, and gradient energy coefficients of the martensite-martensite and austenite-martensite interfaces are estimated for NiAl. Finally, we outline a version of phase field theory for dislocations based on our theoretical framework for phase transformations.

DOI: 10.1103/PhysRevB.68.134201

I. INTRODUCTION

In parts I (Ref. 1) and II (Ref. 2) we developed a fifth-degree polynomial (2-3-4-5) Gibbs (Landau) potential for the description of multivariant stress- and temperature-induced martensitic phase transformations (PT’s) in three dimensions. Our approach was a phenomenological one; that is, the 2-3-4-5 potential was constructed by requiring that it respects the experimentally observed features of martensitic PT’s in shape memory alloys and steels, specifically, constant transformation strain, weakly temperature dependent, or constant, stress hysteresis, and transformation at nonzero tangent elastic moduli. However, the 2-3-4-5 potential is by no means the only Landau potential that satisfies these basic requirements. In this paper, we develop three alternative potentials: namely, a 2-4-6 polynomial in Cartesian order parameters (Sec. II) and two potentials in hyperspherical order parameters (Sec. III). The symmetry requirements for the Gibbs potential (see Sec. IV in Ref. 2) are satisfied for the potentials derived in this paper. The phase equilibrium and transformation conditions for all potentials, including the 2-3-4-5 potential, are identical. Consequently, the geometric representations of the phase equilibrium and transformation conditions introduced in part II Ref. 2 can be used for the alternative potentials as well.

The distinguishing feature of the 2-4-6 polynomial is that its curvature at the martensitic (M) minimum is 4 times larger than at the austenitic (A) minimum, while both curvatures are the same for the 2-3-4-5 polynomial derived in Refs. 1 and 2. This difference in the curvatures significantly modifies the profiles of 2-4-6 critical martensitic nuclei relative to the corresponding profiles for the 2-3-4-5 potential. In contrast to the 2-3-4-5 and 2-4-6 potentials, the hyperspherical potentials have no unphysical local minima and have no constants that do not appear in the phase equilibrium and transformation conditions. Variant-variant transformations occur along the unit hypersphere, whereas the variant-variant transformation paths are much more complicated for the 2-3-4-5 and 2-4-6 polynomial potentials.

It is shown for all potentials that the number of order parameters can be reduced by a factor of 2 if transformation strains for pairs of martensitic variants decompose into two components: one that is the same for both variants and one that is equal in magnitude but of opposite sign for the two variants. This allows us to reduce the number of order parameters by a factor of 2. Examples of applications include cubic-orthorhombic, cubic-monoclinic-I, and cubic-monoclinic-II PT’s and PT’s of invariant-plane-strain (IPS) variants.

In Sec. IV, we compare the 2-3-4-5, 2-4-6, and polar 2-3-4 potentials for the NiAl cubic-tetragonal phase transformation for zero stress and for two three-dimensional stress states.

In Sec. V, analytical solutions of the one-dimensional static Ginzburg-Landau equations for a constant three-dimensional stress tensor and invariant-plane strain are found for the 2-3-4 and 2-4-6 potentials and compared. Analytical solutions of the Ginzburg-Landau equation for the 2-4-6 potential in strain for the stress-free case were found by Falk.5 Jacobs6 generalized some of them to finite strain and to two-dimensional problems that can be treated as one dimensional...
and also calculated displacements. However, the physical interpretation of some of the solutions, such as solitons on \( A \) and \( M \) and soliton splitting, was unclear. In Ref. 7, numerical solutions for critical \( M \) nuclei of the 2-3-4 potential were analyzed in detail under prescribed displacements. It was used in Ref. 7 to model the nonclassical nucleation of an ellipsoidal region.

In contrast to Refs. 5 and 6, our theory incorporates homogeneous multiaxial stresses and we provide physical interpretations of the solutions of the Ginzburg-Landau equations. Despite the significant differences between our theory and Falk’s,\(^5\) the dimensionless forms of the Ginzburg-Landau equations for our 2-4-6 potential and Falk’s strain-based potential coincide. This enables us to borrow some of Falk’s analytical solutions for the stress-free case and analyze their counterparts in relevant variables and under a constant-stress tensor, which is significantly different from Falk’s results. Analytical solutions for the 2-3-4 potential are found. All solutions depend on three parameters: \( s_1 \), which characterizes the stability of austenite; \( s_2 \), which is proportional to the thermodynamic driving force for the \( M \rightarrow A \) PT (both \( s_1 \) and \( s_2 \) are stress and temperature dependent); and the gradient energy coefficient \( \beta \). Phase and transformation diagrams in \( s_1 \)-\( s_2 \) coordinates are analyzed. It is proven by numerical solution of the time-dependent Ginzburg-Landau equation that a stationary \( M \) soliton on \( A \) and an \( A \) soliton on \( M \) are in fact martensitic and austenitic critical nuclei. The structure and energetics of the \( M \) and \( A \) critical nuclei, as well as diffuse \( A \)-\( M \) and \( M \)-\( M \) interfaces, are studied in detail. In particular, the widths of the \( M \) and \( A \) critical nuclei, and the thicknesses of their interfaces, and the energies of the nuclei, and their interfaces are determined in terms of the aforementioned three parameters. A relation between the energy and the width of the equilibrium \( A \)-\( M \) interface and stress hysteresis is found. Two types of \( M \)-\( M \) interfaces are considered: a simple kink connecting \( M \) to \( M \) and an exotic split \( M \)-\( M \) interface comprised of juxtaposed \( M \)-\( A \) and \( A \)-\( M \) interfaces. This splitting is interpreted as a potentially new mechanism: barrierless \( A \) nucleation. Nucleation occurs in the region of stability of \( M \) near the equilibrium \( M \)-\( A \) line. Such nucleation might be found experimentally at the interface between two IPS variants.

In Sec. VI, the gradient energy coefficients, energies, and widths of the \( M \)-\( M \) and \( A \)-\( M \) interfaces are estimated for NiAl alloy.

In Sec. VII, a phase field theory of dislocations is developed. The known theory\(^7\) is based on a formalism similar to phase field theory of martensitic PTs (Ref. 4) and has a similar shortcoming: namely, the equilibrium value of the Burgers vector and the plastic strain depend on stress. We extend our approach developed for PTs to dislocations to eliminate this drawback.

II. SIXTH-DEGREE POLYNOMIAL GIBBS POTENTIAL

In this section we obtain a sixth-degree polynomial Gibbs potential \( G \) that describe PT’s between austenite (\( A \)) and martensitic variants (\( M_i \), \( i = 1, 2, \ldots, n \)) and between martensitic variants. One of the requirements of \( G \) is that it describe PT’s with transformation strains that differ only in sign. This is usually done by means of an even polynomial potential in the strain.\(^6\) The only strain appearing in our Landau potentials is the transformation strain \( \epsilon_t \), but it cannot serve as an order parameter because it does not change with the stress, like the strain does—the transformation strain is fixed for each martensitic variant. To describe a change in sign of the transformation strain, the function \( \phi \) [see Eqs. (1) and (2)] must be odd in the order parameter \( \epsilon \), but the thermal part of the free energy \( f \) must be an even function of \( \eta \).

In Sec. II A we derive a 2-4-6 polynomial potential in order parameters \( \eta_i \in [0, 1] \). In Sec. II B the range of order parameter values is extended from \([0, 1]\) to \([-1, 1]\) for PT’s with \( \epsilon_t \) that differ only in sign and more generally for PT’s where the \( \epsilon_t \) for pairs of martensitic variants decompose into two components: one that is the same for both variants and one that is equal in magnitude but of opposite sign for the two variants. This extension reduces the number of order parameters by a factor of 2. A similar result was obtained for the 2-3-4-5 potential.

A. Positive order parameters

The 2-4-6 polynomial is subject to the same requirements as the 2-3-4-5 polynomial Gibbs potential derived in parts I (Refs. 1) and II (Ref. 2). Following the same steps as before we obtain

\[
G = -\sigma \left( \lambda_0 + \sum_{k=1}^{n} (\lambda_k - \lambda_0) \varphi(a_\lambda, \eta_k) \right) : \sigma / 2
- \sigma \left( \lambda_0 + \sum_{k=1}^{n} (\lambda_0 - \lambda_0) \varphi(a_\lambda, \eta_k) : \sigma \right) : \sigma / 3
- \sigma \left( \lambda_0 + \sum_{k=1}^{n} (\lambda_k - \lambda_k) \varphi(a_\lambda, \eta_k) : \sigma \right) : \sigma / 4
- \sigma \sum_{k=1}^{n} \varphi(a, \eta_k) - \sigma \left( \sigma \sum_{k=1}^{n} \varphi(a, \eta_k) \right) + \sum_{k=1}^{n} f(\sigma, \eta_k) \right)
\]

where

\[
\varphi(a, \eta_k) = a \eta_k^2 / 2 + (3 - a) \eta_k^4 + (a - 4) \eta_k^6 / 2, \quad 0 \leq a \leq 6;
\]

\[
f(\sigma, \eta_k) = A \eta_k^2 / 2 + (3 \Delta G^\theta - A) \eta_k^4 + (A - 4 \Delta G^\theta) \eta_k^6 / 2;
\]

\[
F_{ij}(\eta_i, \eta_j) = B \eta_i^2 \eta_j^2 + (Z_{ij} - B) \eta_i^4 \eta_j^4 + C \eta_i^4 \eta_j^4
+ (Z_{ij} - B) \eta_i^2 \eta_j^4;
\]

for the 2-4-6 polynomial Gibbs potential.
Here \( \sigma \) is the stress tensor, \( e_{ii} \) and \( e_{ij} \) are the transformation and thermal strains of the \( i \)th variant, \( i = 0 \) corresponds to \( A \), \( e_{i0} = 0 \), \( \lambda_i^0 \) is the elastic compliance tensor of order \( k \) for variant \( i \) (\( \lambda_i^0 = \lambda_i^0 \)), and \( \Delta G^0 \) is the difference between the thermal parts of the Gibbs energies of \( M \) and \( A \). The parameters \( \alpha \) and \( \bar{\alpha} \) characterize the thresholds for \( A \rightarrow M_i \) and \( M_j \rightarrow M_i \) transformations, while \( B \) and \( C \) control the Gibbs energy away from both the \( A \) and \( M_i \) minima and the minimum-energy paths between the minima; therefore, they do not affect phase equilibrium and transformation conditions. The material parameters \( a, a_{ij}, a_{ij}, a_{ij} \), and \( a_{ij} \) govern the variations of \( e_{ii} \), \( e_{ij} \), and the elastic compliances between the \( A \) and \( M_i \) minima.

Define \( \eta_i = (0, \ldots, 0, \eta_i = 1, 0, \ldots, 0) \), the vector from the origin to \( M_i \). The Gibbs potential was constructed to have local minima at the origin and at the points \( \eta_i \), \( i = 1, \ldots, n \), but no constraints were placed on \( G \) at the points \( \hat{\eta}_i + \eta_i, \hat{\eta}_i + \eta_i, \ldots, \hat{\eta}_i + \eta_i \), etc. Consequently, \( G \) may be smaller at such points that at the \( A \) and \( M_i \) local minima; i.e., nonphysical phases can appear. The relative values of \( G \) at \( A \), \( M_i \), \( \hat{\eta}_i + \eta_i \), etc., are controlled by the parameters \( B \) and \( C \). Since \( F_{ij}(1,1) = Z_{ij} + Z_{ji} - B + C \), the elimination of minima at \( \hat{\eta}_i + \eta_i, \hat{\eta}_i + \eta_i, \ldots, \hat{\eta}_i + \eta_i \), etc., can be achieved by choosing \( B \leq 0 \) and \( C > 0 \).

Define \( \bar{0} = (0, \ldots, 0) \), which corresponds to \( A \), and \( \bar{\eta}_i = (0, \ldots, 0, \bar{\eta}_i, 0, \ldots, 0) \). The phase transformation conditions are as follows:

\[ A \rightarrow M_i : \]

\[
\frac{\partial^2 G(\sigma, \theta, \eta_i)}{\partial \eta_i} \leq 0
\]

\[
\Rightarrow a \sigma : e_{ii} + a_{ij} \sigma : (e_{ij} - e_{ij}) + \frac{a_{ij}}{2} \sigma : (\lambda_i - \lambda_0) : \sigma
\]

\[
+ \frac{a_{ij}}{3} \sigma : ((\lambda_i^3 - \lambda_0^3) : \sigma)
\]

\[
+ \frac{a_{ij}}{4} \sigma : ((\lambda_i^3 - \lambda_0^3) : \sigma) : \sigma \equiv A;
\]

\[ M_i \rightarrow A : \]

\[
\frac{\partial^2 G(\sigma, \theta, \eta_i)}{\partial \eta_i} \leq 0
\]

\[
\Rightarrow (6-a) \sigma : e_{ii} + (6-a_{ij}) \sigma : (e_{ij} - e_{ij})
\]

\[
+ \frac{6-a_{ij}}{2} \sigma : (\lambda_i - \lambda_0) : \sigma
\]

\[
+ \frac{6-a_{ij}}{3} \sigma : ((\lambda_i^3 - \lambda_0^3) : \sigma)
\]

\[
+ \frac{6-a_{ij}}{4} \sigma : ((\lambda_i^3 - \lambda_0^3) : \sigma) : \sigma \equiv 6 \Delta G^0 - A;
\]

\[ M_i \rightarrow M_j : \]

\[
\frac{\partial^2 G(\sigma, \theta, \eta_i)}{\partial \eta_j} = -6 \sigma : e_{ii} - 6 \sigma : (e_{ij} - e_{ij})
\]

\[
- 3 \sigma : (\lambda_i - \lambda_j) : \sigma - 2 \sigma : ((\lambda_j^3 - \lambda_i^3) : \sigma)
\]

\[
\leq 3 \sigma : (\lambda_j^3 - \lambda_i^3) : \sigma \leq 2 \bar{\alpha} \leq 0.
\]

The transformation strain is equal to \(- \partial G(0, \theta, \eta_i)/\partial \sigma \) at zero thermal strain:

\[
e_i = \sum_{i=1}^{n} e_{ii} \varphi(\eta_i, \eta_i) - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \eta_i^2 \eta_j^2 \eta_i^2 \eta_j^2 \eta_i^2 \eta_j
\]

\[
+ (a-3) \left( \eta_i^2 e_{ii} + \eta_i^2 e_{ii} \right).
\]

It is easily verified that \( e_i \) satisfies all requirements: \( e_i(\bar{0}) = 0 \), \( e_i(\eta_i) = e_{ii} \), \( e_i(\eta_i) = e_{ii} \varphi(\eta_i, \eta_i) \).

The thermodynamic equilibrium conditions \( G / \eta_i = 0 \) (\( i = 1, \ldots, n \)) have \( n+1 \) solutions corresponding to \( A \) and the \( M_i \): \( \eta = \bar{0} \) and \( \eta = \eta_i, i = 1, \ldots, n \). There are other solutions of \( G / \eta_i = 0 \) that correspond to maxima or saddle points. In the case of a single variant, there is, in addition to the extrema at \( \eta_i = 0 \) and \( \eta_i = 1 \), an extremum at

\[
\eta_3 = \left[ A - a \sigma : e_{ii} + a_{ij} \sigma : e_{ij} + \Lambda \right] / 3 \bar{h},
\]

\[
A := a_{ij} \sigma : (\lambda_i - \lambda_j) : \sigma + 2 \sigma : ((\lambda_j^3 - \lambda_i^3) : \sigma) : \sigma / 3
\]

\[
+ a_{ij} \sigma : (\lambda_j^3 - \lambda_i^3) : \sigma) : \sigma / 4,
\]

\[
h := A - 4 \Delta G^0 - (a - 4) \sigma : e_{ii} + (a_{ij} - 4) \sigma : e_{ij} + \Lambda / 4,
\]

\[
+ (a_{ij} - 4) \sigma : (\lambda_i - \lambda_j) : \sigma / 2
\]

\[
+ (a_{ij} - 4) \sigma : ((\lambda_j^3 - \lambda_i^3) : \sigma) / 3
\]

\[
+ (a_{ij} - 4) \sigma : ((\lambda_i^3 - \lambda_j^3) : \sigma) / 4.
\]
Designating the critical temperature at which stress-free A and M. The activation barrier for the A→M PT can be calculated by substituting η₁ in Eq. (1):

\[ G(\sigma, \theta, \eta_1) = G(\sigma, \theta, 0) - G(\sigma, \theta, 1), \]

which corresponds to a maximum in G if η₁ < 1. The height of the activation barrier for the A→M PT can be obtained by adding G(\sigma, \theta, 0) − G(\sigma, \theta, 1) = \alpha(\eta_1^4/6 - \Lambda^2\eta_1^2/3).

The activation barrier for the M→A PT is given by Eq. (1) for PT’s that can be treated as one dimensional, i.e., \( A_{0} < 6z \) was assumed in the derivation of the equation for \( \tilde{\theta} \). It is a good approximation over a modest range of temperatures to take \( \Delta G^0 \) and A to be linear functions of the temperature. \( \Delta G^0 = z(\theta - \theta_c), \ A = A_0(\theta - \theta_c), \ z > 0, \ A_0 > 0, \)

where \( \theta_c \) is the equilibrium temperature for stress-free A and M. \( -z \) is the jump in specific entropy at the equilibrium temperature, and \( \theta_c \) is the critical temperature at which stress-free A loses its thermodynamic stability. Then

\[ f = A_0(\theta - \theta_c) \eta^2/2 + [3\tilde{z}(\theta - \theta_c) - A_0(\theta - \theta_c)] \eta^3/6. \]

Designating the critical temperature at which stress-free M loses its thermodynamic stability as \( \tilde{\theta}_c \), one obtains \( \tilde{\theta}_c = \theta_c + 6\tilde{z}(\theta_c - \theta_c)/(6\tilde{z} - A_0) \) with \( A_0 < 6\tilde{z} \) from Eq. (6). The inequality \( A_0 < 6\tilde{z} \) was assumed in the derivation of the equation for \( \tilde{\theta}_c \) and it follows from the evident inequalities \( \tilde{\theta}_c > \theta_c > \theta_0 \) that it is not contradictory. For equal deviations of the critical temperatures from the equilibrium temperature at various stresses for the 2-3-4-5 potential, \( \eta_3 < 1 \), \( A_0 = 100 \) K, \( \theta_c = 200 \) K, and \( A_0 = 0.3 \) MPa/K were used for both plots.

\[ H = \frac{3(\tilde{A}_0 - \tilde{z}a) \tilde{\theta}_c + 3\tilde{z}(\theta_c - \tilde{\theta}_c)}{a(6 - a)\tilde{\eta}(\tilde{\eta} - a)} \tilde{\eta}^3/3. \]

This expression for \( H \) is the same as for the 2-3-4-5 potential. For \( A_0 > \tilde{z}a \), the hysteresis grows (decreases) with temperature and \( A_0 = \tilde{z}a \) is independent of temperature.

The equation \( \epsilon = -\partial G/\partial \sigma \) gives the relation between strain and order parameters for any actual transformation path at constant \( \sigma \). Consider a single martensitic variant. In thermodynamic equilibrium, \( \epsilon(\sigma, \eta) = -\partial G/\partial \sigma \) and (9) for \( \eta(\sigma) \) constitute a parametric relation between strain and order parameter with \( \sigma \) as the parameter. This \( \epsilon-\eta \) relation simplifies considerably in a linear elastic material for which Eq. (13) holds:

\[ \epsilon = \epsilon, \phi(\sigma, \eta) + \lambda(\epsilon - \eta) = \frac{3(\tilde{A}_0 - \tilde{z}a) \tilde{\theta}_c + 3\tilde{z}(\theta_c - \tilde{\theta}_c)}{a(6 - a)\tilde{\eta}(\tilde{\eta} - a)} \tilde{\eta}^3/3. \]

FIG. 1. G(\eta) for equal deviations of the critical temperatures from the equilibrium temperature at various stresses for (a) \( \theta = 200 \) K and (b) \( \theta = 250 \) K. The same parameter values—namely \( \epsilon_1 = 0.1, \ a = 3, \ \theta_c = 100 \) K, \( \theta_c = 200 \) K, and \( \tilde{A}_0 = 0.3 \) MPa/K—were used for both plots.
sion to negative $\eta$ will be considered in Sec. II B. In contrast to the 2-3-4-5 polynomial (see Fig. 6 in Ref. 1), the curvature (second derivative with respect to $\eta$) at the martensitic minimum is significantly larger than at the austenitic minimum. Indeed, the ratio \(\left(\frac{\partial^2 G(1)}{\partial \eta^2}\right)/\left(\frac{\partial^2 G(0)}{\partial \eta^2}\right)\) for the 2-4-6 potential is 4 times greater than for the 2-3-4-5 polynomial. (Note that the curvatures of the $A$ and $M$ minima are the same for the 2-3-4-5 potential at thermodynamic equilibrium.) This difference is not related to differences in the elastic moduli or to the conditions for the loss of stability of homogeneous phases. This difference in curvature leads to significant differences between the profiles and energies of the critical martensitic nuclei for the 2-4-6 and 2-3-4 potentials (see Sec. V). It also leads to the solutions of the time-dependent Ginzburg-Landau equations to different equilibrium domain wall configurations for the same thermodynamic, initial, and boundary conditions, which will be described in detail elsewhere.

The stress-strain curve for the 2-4-6 polynomial is similar to that of the 2-3-4-5 polynomial, but there are differences; see Fig. 5 in Ref. 1. First, for $a = 3$, $\sigma$ is a linear function of $\eta$ for the 2-3-4-5 polynomial, but $\sigma$ is a nonlinear function of $\eta$ for the 2-4-6 polynomial. The absolute value of the tangent elastic modulus at $\eta = 0$ is much larger for the 2-4-6 polynomial than for the 2-3-4-5 polynomial, a consequence of the greater curvature of $G(\eta)$ at $\eta = 1$.

B. Continuation of the 2-4-6 order parameters to negative values

Continuation of the order parameters to negative values requires that the term $C \eta^i \eta^j$ in $F_{ij}$ be replaced by $C \eta^i \eta^j \eta^k$. Then $F_{ij}$ is invariant under $\eta_i \rightarrow -\eta_i$ or $\eta_j \rightarrow -\eta_j$ and spurious minima at $\pm \eta_i \pm \eta_j$, $\pm \eta_i \pm \eta_j$, $\pm \eta_j$, etc., can be eliminated by choosing $B \leq 0$ and $C > 0$, as is the case for positive order parameters.

We start with the special case of martensitic variants with transformation strains that differ only in sign. This can be the case only if the transformation strain is purely deviatoric since the volumetric strains must be of the same sign. This condition is approximately met for the IPS variants in, for example, CuAlNi, CuZnGa, CuZn, CuAlZn, AgCd, and NiAl alloys. These pairs of elastic variants with $\epsilon_i$ of opposite sign, $M_+ \epsilon_i$ and $M_- \epsilon_i$, have equal elastic compliances. The strain tensors will be treated below. Our 2-4-6 Landau potential, Eqs. (1)–(5), can be modified to describe transformations between $M$ and $n$ IPS variants and among $n$ IPS variants with $n/2$ order parameters. A single order parameter is associated with $M_+$ and $M_-$; the variants are located at $\pm \eta_i$ for some $i$. The modified form of the 2-4-6 potential is obtained by substituting $\epsilon_i \text{sgn}(\eta_i)$ for $\epsilon_i$ and $n/2$ for $n$. The sign function $\text{sgn}(\eta_i) = \eta_i/|\eta_i|$ is always multiplied by $\eta_i^m$, where $2 \leq m \leq 6$. The second derivatives of the quadratic terms include terms of the form $2 \text{sgn}(\eta_i)$; therefore, $\partial^2 G/\partial \eta^2$ is discontinuous at the origin; $G$ and $\partial G/\partial \eta$ are continuous at the origin.

Let us consider for simplicity $\eta$-independent elastic compliances. For just two IPS variants $M_+$ and $M_-$, the equilibrium condition $\partial G/\partial \eta = 0$ gives, in addition to the roots $\eta_1 = 0$, $\eta_2 = 0$, and $\eta_3$ [see Eq. (9)], the negative roots

$$
\eta_4 = -1, \quad \eta_5 = -\sqrt{\frac{a \sigma \epsilon_i + A}{3[(a - 4) \sigma \epsilon_i - 4 \Delta G^\theta + A]}}.
$$

(17)

The PT conditions, which follow from $\eta_4 = 0, 1$ and $\eta_5 = 0, -1$, are

$$
A \rightarrow M_+: \quad \sigma \epsilon_i \geq \frac{A}{a}; \quad A \rightarrow M_-: \quad \sigma \epsilon_i \leq -\frac{A}{a};
$$

$$
M_+ \rightarrow A: \quad \sigma \epsilon_i \leq \frac{6 \Delta G^\theta - A}{6 - a};
$$

$$
M_- \rightarrow A: \quad \sigma \epsilon_i \geq -\frac{6 \Delta G^\theta - A}{6 - a}.
$$

(18)

For $\Delta G^\theta > A(a - 3)/3a$, the $M_- \rightarrow A$ PT occurs at smaller stresses than does the $A \rightarrow M_+$ PT; for $a = 3$ this occurs at $\theta > \theta_e$. In this case $M_-$ first transforms to $A$ and then, after an increase in stress or a decrease in temperature, $A$ transforms to $M_+$. In the opposite case, $M_+$ transforms directly to $M_-$. Because $A$ is unstable.

A volume preserving IPS is a simple shear in direction $m$ in the habit plane with normal $\eta$, $\epsilon_i = \frac{1}{2} \gamma_1 (m n_i + n m_i)$, $\sigma \epsilon_i = \gamma_1$, $\tau = m \tau \cdot n$; here $\tau$ and $\gamma_1$ are the shear stress and strain. The one-dimensional treatment presented in Ref. 1 is applicable.

In Fig. 1, the dependence of $G = G + \frac{1}{2} \sigma \epsilon_i \cdot \epsilon_i \eta_i$ on $\eta$ in the interval $[-1, 1]$ is presented for two temperatures and various stresses for $A_0 = 3 \gamma_1$.

If part $\epsilon_i$ of the transformation strain is the same for the $M$ and $M_-$ variants and another part $\bar{\epsilon}_i$ is of opposite sign, then both $M_+$ and $M_-$ can be described by the single order parameter $\eta$ upon substituting $\epsilon_i + \bar{\epsilon}_i \text{sgn}(\eta_i)$ for $\epsilon_i$ in Eqs. (1) and (5). For IPS, $\epsilon_i = \eta n_i$, and $\bar{\epsilon}_i = \frac{1}{2} \gamma_i (m n_i + n m_i)$, where $\epsilon_i$, the strain normal to the habit plane, is equal to the volumetric strain. The thermal strain tensor may be similarly decomposed, $\epsilon_i = \epsilon_i^{\text{dev}} + \epsilon_i^{\text{vol}}$, where $\epsilon_i^{\text{dev}}$ and $\epsilon_i^{\text{vol}}$ are the deviatoric and volumetric parts of $\epsilon_i$. For the cubic-orthorhombic PT (e.g., Cu-Ni-Al and Au-Cd alloys) and the cubic-monoclinic-II PT (e.g., Cu-Zn-Al alloys), $\epsilon_i$ describes the diagonal components of $\epsilon_i$ and $\bar{\epsilon}_i$ corresponds to the only shear component. The order parameters are needed to describe the six martensitic variants in the first case and six order parameters are required to describe the 12 variants in the second case. For the cubic-monoclinic-I PT (e.g., Ni-Ti alloys), $\bar{\epsilon}_i$ is associated with one shear and the three diagonal components of $\epsilon_i$ and $\bar{\epsilon}_i$ is associated with the other two shear components.

Note that a similar procedure for number of degrees of freedom by a factor of 2 can be followed for
the 2-3-4-5 polynomial. In addition to substituting \( \tilde{e}_i \) 
and \( \tilde{e}_i \text{sgn}(\eta_i) \) for \( e_i \), one needs to substitute \( |\eta_i| \) for \( \eta_i \) for all odd powers of \( \eta_i \).

### III. Potentials in Hyperspherical Coordinates

In the \( n \)-dimensional space of order parameters, all martensitic variants are located on the unit hypersphere; thus it is natural to construct Gibbs potentials using the hyperspherical order parameters \( r \) and \( \psi_k \), \( k = 1, \ldots, n \). Here \( r \) is the radial coordinate in order-parameter space and \( \pi \psi_k / 2 \) is the angle between the radius vector \( r \) and the \( \eta_k \) axis:

\[
r = \left( \sum_{i=1}^{n} \eta_i^2 \right)^{1/2}, \quad 0 \leq \psi_k = \frac{2}{\pi} \cos^{-1} \frac{\eta_k}{r} \leq 1, \\
\sum_{k=1}^{n} \cos^2 \left( \frac{\pi}{2} \psi_k \right) = 1.
\]

The third equation is a constraint that can be eliminated by expressing \( G \) in terms of the \( \eta_k \). New Gibbs potentials in \( r \) and \( \psi_k \) can be derived from our 2-3-4 and 2-4-6 potentials \( G(r) \) for a single martensitic variant by allowing for \( \psi_k \)-dependence in the transformation strain and including a term that introduces \( \psi_k \)-dependent barriers between all variants. We emphasize that the potentials in hyperspherical coordinates are not simply reparametrizations of the 2-3-4 and 2-4-6 potentials in Cartesian coordinates but rather new potentials with somewhat different physics. In contrast to the 2-3-4 and 2-4-6 potentials, the Gibbs potentials in \( r \) and the \( \psi_k \) have the following desirable features:

(i) They have no unphysical minima and no constants that do not appear in the phase equilibrium and transformation conditions.

(ii) The paths of minimum free energy between variants are great circles on the unit hypersphere. Variant-variant transformations occur along these paths and can be parameterized by a single angle. This property of a potential in hyperspherical coordinates makes it possible to obtain an analytical kink solution of the time-independent Ginzburg-Landau equation that connects martensitic variants without passing through an austenitic minimum. Similar solutions cannot be obtained for the potentials in Cartesian order parameters.

#### A. Two martensitic variants

We now consider the case \( n = 2 \) for \( \eta \)-independent elastic compliances and thermal strain tensor. A polar coordinate system can be used and all derivations are quite simple. Our Gibbs potential is given by

\[
G(\sigma, \theta, r, \psi) = -\sigma \lambda \cdot \sigma / 2 - \sigma \cdot (e_{12} - e_{11}) P(\psi) \varphi_p(r) \\
+ f_p(\theta, r) + \bar{A} Q(\psi) q_p(r).
\]

where \( p = 4 \) corresponds to the 2-3-4 polynomial, \( p = 6 \) corresponds to the 2-4-6 polynomial, and \( \psi_1 = 1 - \psi_2 \). For \( p = 4 \) we have

\[
\varphi_d(r) = ar^2 + (4 - 2a)r^3 + (a - 3)r^4, \quad 0 < a < 6,
\]

\[
f_d(\theta, r) = Ar^2 + (4AG - 2A)r^3 + (A - 3AG)r^4,
\]

and for \( p = 6 \) see Eqs. (2) and (3) with \( r \) substituted for \( \eta_k \). The functions \( P, Q, q \) are to be determined. The requirement that \( G \) give the free energies of \( M_1 \) and \( M_2 \) at \( \psi = 0 \) and \( \psi = 1 \), respectively, implies the conditions

\[
P(0) = 0, \quad P(1) = 1, \quad Q(0) = Q(1) = 0.
\]

Without loss of generality we assume \( q(1) = 1 \). We require the radial derivative of \( G(r, \psi) \) to vanish at the origin and at \( r = 1 \) for \( 0 \leq \psi \leq 1 \):

\[
\frac{\partial G(0, \psi)}{\partial r} = \frac{\partial G(1, \psi)}{\partial r} = 0 \Rightarrow \frac{d q(0)}{d r} = \frac{d q(1)}{d r} = 0.
\]

Similarly, the \( \psi \) derivative of \( G(r, \psi) \) is forced to vanish at all \( r \) for \( \psi = 0, 1 \):

\[
\frac{\partial G(0, \psi)}{\partial \psi} = \frac{\partial G(1, \psi)}{\partial \psi} = 0 \Rightarrow \frac{d P(0)}{d \psi} = \frac{d P(1)}{d \psi} = 0, \quad \frac{d Q(0)}{d \psi} = \frac{d Q(1)}{d \psi} = 0.
\]

These conditions include the equilibrium conditions \( \partial G(\eta_k) / \partial \eta_k = 0 \) (\( i, j \neq 1 \)) and also impose additional constraints on the form of the potential. Requiring that the inequality

\[
\partial^2 G(\psi) / \partial \psi^2 = -\sigma(c_{12} - c_{11}) d^2 P / d \psi^2 + \bar{A} d^2 Q / d \psi^2 \leq 0
\]

for \( \psi = 0 \) (\( \psi = 1 \)) coincide with Eq. (6) in part II (Ref. 2)—i.e., it give the same \( M_1 \rightarrow M_2 \) (\( M_2 \rightarrow M_1 \)) PT criterion as Eq. (7) or (5) in (Ref. 2)—results in

\[
\partial^2 P(0) / \partial \psi^2 = -\partial^2 P(1) / \partial \psi^2 = 6,
\]

\[
\partial^2 Q(0) / \partial \psi^2 = \partial^2 Q(1) / \partial \psi^2 = 2.
\]

We also require \( \lim_{\rho \to 0}(q(\rho^2)) = \lim_{\rho \to 0}(q(\rho r^2)) = 0 \), which eliminates the barrier to the \( M_1 \rightarrow M_2 \) PT in the vicinity of the origin. Otherwise, following \( M_2 \rightarrow A \), the \( A \) remembers the variant from which it came. Restricting our attention to 2-3-4 and 2-4-6 polynomials, we obtain the following functions which satisfy the above requirements:

\[
Q = \psi^2(1 - \psi^2), \quad P = \psi^2(3 - 2\psi),
\]

\[
q_4 = 4r^3 - 3r^4, \quad q_6 = 3r^4 - 2r^6.
\]

The polynomials \( q, f, \) and \( \varphi \) must be of the same degree. If this were not the situation, then additional unphysical extrema might appear and an analytical study would not be possible. The polynomials in \( \psi \) can be used with both fourth- and sixth-degree polynomials in \( r \). Note that \( Q \) can be written in the form \( Q = \psi_i^2 \psi_i^2 \). For \( n \) martensitic variants, this generalizes to \( Q = \psi_i^2 \cdot \psi_i^2 \); see next section.
Variant-variant transformations can be studied analytically by putting $r = 1$ in the above equations. For example, a solution of the equation $\partial G(1, \psi) / \partial \psi = 0$ is $\psi_1 = 1/2 - (3S)/(2A)$ with $S = \alpha_p (e_{ij} - e_{ii})$, which is the location of the barrier for the $M_1 \rightarrow M_2$ PT. The corresponding activation barriers are

\begin{align}
G(1, \psi_3) - G(1,0) &= (1 - 3S/\bar{A})(\bar{A} + S)/16, \\
G(1, \psi_3) - G(1,1) &= (1 + 3S/\bar{A})(\bar{A} - S)/16.
\end{align}

A variant-variant kink solution of the time-independent Ginzburg-Landau equation for the $r = 1$ potential will be obtained in Sec. V.

**B. n martensitic variants**

We assume $\eta$-independent elastic compliances and thermal strain. Equations (20) and (27) generalize to

\begin{equation}
G + \frac{1}{2} \alpha \varphi \lambda \varphi = - \alpha \sum_{k=1}^{n} e_{ik}(1 - 3 \psi_k^2 + 3 \psi_k^3) \varphi_p(r)
+ f_p(\theta, r) + \bar{A} \prod_{k=1}^{n} \psi_k^3 q_p(r).
\end{equation}

It is easy to check using $\psi_1 + \psi_2 = 1$ that, for $n = 2$, Eq. (29) reduces to Eq. (20) with $P$ and $Q$ given by Eq. (27).

We now verify the equilibrium conditions—namely, $\partial G / \partial \eta_i = 0$—at the points $0 = (0, \ldots, 0)$ and $\hat{\eta}_j$, $j = 1, \ldots, n$, as well as the phase instability conditions:

\begin{align}
M_j \rightarrow A: & \quad \alpha e_{ii} \leq \frac{6 \Delta G^g - A}{6 - a}, \\
A \rightarrow M_j: & \quad \alpha e_{ii} \geq \frac{A}{a}.
\end{align}

These conditions are most easily verified by first expanding the potentials (29) around the points $\hat{\eta}_j$ and $\bar{\eta}$ to second order in the order parameters and then calculating the derivatives.

In the neighborhood of $\hat{\eta}_j$ the potential is

\begin{equation}
G = \Delta G^g - \frac{1}{2} \alpha \varphi \lambda \varphi - \alpha \varphi e_{ij} + \frac{4}{\pi^2} \sum_{i \neq j} [3 \alpha_p (e_{ij} - e_{ii}) + \bar{A}] \eta_i^2
+ \omega_p [(6 - a) \alpha_p e_{ij} + A - 6 \Delta G^g] (\eta_j - 1)^2 + O(\eta^3),
\end{equation}

where $\omega_4 = 1$ and $\omega_6 = 2$. This always has an extremum at $\hat{\eta}_j$:

\begin{equation}
\frac{\partial G(\hat{\eta}_j)}{\partial \eta_i} = 0, \quad i, j = 1, \ldots, n.
\end{equation}

The mixed derivatives $\partial^2 G / \partial \eta_i \partial \eta_j (i \neq j)$ of Eq. (33) vanish at all $\hat{\eta}_i$. It follows that the conditions $\partial^2 G(\hat{\eta}_j)/\partial \eta_i^2 \leq 0$ and $\partial^2 G(\hat{\eta}_j)/\partial \eta_i^2 \geq 0$ are the conditions for $M_j \rightarrow A$ and $M_j \rightarrow M_i$, respectively. The $M_j \rightarrow A$ PT condition is given by

\begin{equation}
\frac{\partial^2 G(\hat{\eta}_j)}{\partial \eta_i^2} = 2 \omega_p [(6 - a) \alpha_p e_{ij} + A - 6 \Delta G^g] \leq 0,
\end{equation}

which coincides with Eq. (30). Similarly, the $M_j \rightarrow M_i$ PT condition is

\begin{equation}
\frac{\partial^2 G(\hat{\eta}_j)}{\partial \eta_i^2} = \frac{8}{\pi^2} [3 \alpha_p (e_{ij} - e_{ii}) + \bar{A}] \leq 0,
\end{equation}

in agreement with Eq. (32).

In the neighborhood of the origin we have

\begin{equation}
M_j \rightarrow M_i: \quad 3 \alpha_p (e_{ij} - e_{ii}) + \bar{A} \leq 0.
\end{equation}

\begin{figure}[h]
\centering
\includegraphics{fig2a.png} \quad \includegraphics{fig2b.png} \quad \includegraphics{fig2c.png}
\caption{Level curves of $G$ for NiAl at $\theta = 0$ and normal stresses $\sigma_1 = \sigma_2 = \sigma_3 = 0$: (a) 2-3-4 polynomial in polar coordinates, (b) 2-3-4 polynomial in Cartesian coordinates, and (c) 2-4-6 polynomial in Cartesian coordinates.}
\end{figure}
FIG. 3. Level curves of $\tilde{G}$ for NiAl at $\theta=0$ and normal stresses $\sigma_1=1000$, $\sigma_2=-1000$, $\sigma_3=-3000$: (a) 2-3-4 polynomial in polar coordinates, (b) 2-3-4 polynomial in Cartesian coordinates, and (c) 2-4-6 polynomial in Cartesian coordinates.

\[ G = -\frac{1}{2} \sigma : \chi \sigma + \omega_p^{-1} \left[ -a \sigma \sum_{k=1}^{n} \varepsilon_{ik} (1 - 3 \psi_k^2 + 2 \psi_k^3) + A \right] r^2 \]

(37)

for the variant with the maximum value of $\sigma : \varepsilon_{ij}$, in agreement with Eq. (31).

Thus, the potential (29) in hyperspherical coordinates satisfies the equilibrium and PT conditions.

If $\tilde{\varepsilon}_{ii}$ is the same for $M_+$ and $M_-$ variants and $\tilde{\varepsilon}_{ii}$ is of opposite sign, then the number of order parameters is reduced by a factor of 2 by substituting $\tilde{\varepsilon}_{ii} + \tilde{\varepsilon}_{ij} \text{sgn} (\eta_i)$ for $\varepsilon_{ij}$ in Eq. (29).

FIG. 4. Level curves of $\tilde{G}$ for NiAl at $\theta=0$ and normal stresses $\sigma_1=4051$, $\sigma_2=-2000$, $\sigma_3=-3000$: (a) 2-3-4 polynomial in polar coordinates, (b) 2-3-4 polynomial in Cartesian coordinates, and (c) 2-4-6 polynomial in Cartesian coordinates.
the tensors $e_{ij}$ and $e_{ij}$ can be obtained by permutation of components. The constant $D$ does not appear in the polar potential. We chose $C = -1000$ from the condition that at $\sigma = -7000$ MPa, which is far outside the region of stability of the martensite and consequently far beyond stresses of interest, $G(\sigma,0,1,0) \gg G(\sigma,0,1,0)$, and no unphysical minima exist. This ensures that the same is true at smaller compressive stresses or in tension.

Plots of $\tilde{G}(\sigma, \theta, \eta_1, \eta_2) = G(\sigma, \theta, \eta_1, \eta_2) + 1/2 \sigma: \lambda: \sigma$ for PT's in NiAl for zero stress and two three-dimensional stress states at $\theta = 0$ K for the 2-3-4-5, 2-4-6, and polar 2-3-4 potentials are shown in Figs. 2–4. The normal stresses on the faces of the crystal are denoted $\sigma_i$; all stresses are in MPa.

We applied a large compressive stress $\sigma_3$ to suppress the appearance of the third variant. Growth of $\tilde{G}$ corresponds to variation from black to white. The driving force is orthogonal to the level curves. There are no unphysical minima present. This is particularly noteworthy for the polar 2-3-4 potential since it contains no constants that can be tuned to eliminate unphysical minima. We also checked this for the three-variant case by analyzing $\tilde{G}$ numerically.

For zero stresses (Fig. 2), both $M$ variants are stable and $A$ is metastable.

For $\sigma_1 = -\sigma_2 = 1000$ (pure shear in the 1-2 plane), $\sigma_3 = -3000$, $M_1$ is stable, $M_2$ is metastable, and $A$ is unstable (Fig. 3). Because of a barrier between $M_2$ and $A$, $A$ transforms to $M_1$ only.

For $\sigma_1 = 4051$, $\sigma_2 = -2000$, and $\sigma_3 = -3000$, $M_1$ is stable, and $M_2$ is unstable only in the direction of $M_1$ because the barrier between $M_2$ and $A$ still exists (Fig. 4).

The energy variation along the coordinate axes is identical for the 2-3-4-5 potential and the polar 2-3-4 potential. The differences between these potentials are most pronounced for the stress-free case. Because the 2-4-6 potential has a much larger curvature at the $M$ minimum than at the $A$ minimum, there are significant differences in local values between the 2-4-6 and the other two potentials near the stable $M$ minimum. As will be shown in Sec. V, such local differences result in different profiles for the critical $M$ nuclei.

V. CRITICAL NUCLEI AND DIFFUSE INTERFACES

In this section we will obtain and interpret some spatially one-dimensional analytical solutions of the time-independent Ginzburg-Landau equations for the 2-3-4, 2-4-6, and $r\psi_k$ potentials. As was shown in Ref. 6, some two-dimensional problems for the cubic-rectangular PT can be treated as one dimensional, which is the case for our models as well. Our one-dimensional results on critical nuclei and diffuse interfaces hold for IPS variants—that is, for transformation strains of the form $e_{ij} = 1/2 \gamma_{ij}(\mathbf{m} \cdot \mathbf{m}) \text{sgn}(\eta) + \epsilon \mathbf{m}$, where $\gamma_{ij}$ is a tensor, $\epsilon \mathbf{m}$ is a constant, and $\text{sgn}(\eta)$ is a sign function.

For zero stresses ($\sigma = 0$), the order parameter is a function of the coordinate $x$ along the $n$ axis. Despite the restriction to one spatial dimension, our solutions are valid for an arbitrary three-dimensional homogeneous stress tensor $\sigma$ in a rectangular parallelepiped with corresponding homogeneous tractions at its faces. In order to impose the usual boundary condition on the order parameter [see Eq. (55)], the faces of the parallelepiped must be orthogonal and parallel to $\sigma$ (Fig. 5). In the following subsections the parallelepiped is actually infinite in the $x$ direction.

A. Governing equations

We write the 2-4-6 and 2-3-4 potentials in terms of two parameters.

$$ G_6 = s_1 \eta^2 [1 - (4 - P) \eta^2/2 + (3 - P) \eta^4/3]/2, $$

$$ G_4 = s_1 \eta^2 [1 - (6 - P) \eta^3/3 + (4 - P) \eta^4/4], $$

$$ s_1 = A - a \sigma: \epsilon_1, \quad s_2 = 12(\Delta G^0 - \sigma: \epsilon_1), \quad P = s_2/s_1, $$

Here and later the subscripts 4 and 6 refer to 2-3-4 or 2-4-6 potentials, respectively. We have

$$ \frac{\partial G_6}{\partial \eta} = -s_1 \eta(1 - \eta^2)(3 - P) \eta^2 - 1, $$

$$ \frac{\partial^2 G_6}{\partial \eta^2} = s_1 \eta(1 - \eta)[2 - (4 - P) \eta]; $$

$$ \frac{\partial^2 G_6(0)}{\partial \eta^2} = (1/2) \frac{\partial^2 G_4(0)}{\partial \eta^2} = s_1, $$

$$ \frac{\partial^2 G_6(1)}{\partial \eta^2} = 2 \frac{\partial^2 G_4(1)}{\partial \eta^2} = 2s_1(2 - P); $$

$$ \eta_{\text{max}} = \sqrt{\frac{1}{3 - P}}, \quad \tilde{G}_6(\eta_{\text{max}}) = \frac{s_1}{12} \frac{8 - 3P}{(P - 3)^2}; $$

$$ \eta_{\text{max}} = \frac{2}{4 - P}, \quad \tilde{G}_4(\eta_{\text{max}}) = \frac{4}{3} \frac{s_1(3 - P)}{(4 - P)^3}. $$

Here $\eta_{\text{max}}$ and $\eta_{\text{max}}$ correspond to the maxima of $\tilde{G}$, as in Eq. (9).

For a single order parameter $\eta$ that depends only on the coordinate $x$ along the normal to the habit plane, the Ginzburg-Landau energy $G_{\text{GL}} = G + \nabla \eta \mathbf{\beta} \cdot \nabla \eta$ reduces to $G_{\text{GL}} = G + \mathbf{\beta} (\partial \eta/\partial x)^2$, where the scalar $\mathbf{\beta}$ is a linear combination of components of the second-rank tensor $\mathbf{\beta}$ in the crystal coordinates. Thus, even for a highly anisotropic $A$.
lattice, the one-dimensional case under consideration requires only a single gradient parameter $\beta$. The Ginzburg-Landau energy $G_{GL}$ leads to the time-dependent Ginzburg-Landau equation

$$\frac{\partial \eta}{\partial t} = -\lambda \frac{\partial G_{GL}}{\partial \eta} = -\lambda \left( \frac{\partial G}{\partial \eta} - 2 \beta \frac{\partial^2 \eta}{\partial \xi^2} \right).$$

(44)

Here $\lambda > 0$ is the kinetic coefficient. We rescale variables to cast Eq. (44) in dimensionless form. The dimensionless potentials and order parameters are

$$g_6 = m_6 \tilde{G}_6 = B_6 \xi_6^2 - \xi_6^4 + \xi_6^6, \quad \xi_6 = k_6 \eta;$$

(45)

$$g_4 = m_4 \tilde{G}_4 = B_4 \xi_4^2 - \xi_4^4 + \xi_4^6, \quad \xi_4 = k_4 \eta.$$  

(46)

The parameters are defined and related as follows:

$$B_6 = \frac{4(3-P)}{3(4-P)^2}, \quad k_6 = \sqrt{\frac{2}{3}} \sqrt{\frac{3-P}{4-P}},$$

$$m_6 = \frac{16(3-P)^2}{9 s_1 (4-P)^3} = \frac{2 k_6^2 B_6}{s_1};$$

(47)

$$B_4 = \frac{9(4-P)}{4(6-P)^2}, \quad k_4 = \frac{3}{4} \frac{(4-P)}{(6-P)},$$

$$m_4 = \frac{81(4-P)^3}{64 s_1 (6-P)^4} = \frac{k_4^2 B_4}{s_1}.$$  

It is easy to check that $k$ can be determined by the condition $dg/d\xi = 0$ at the martensitic minimum. Plots of $B(P)$, $k(P)$, and $s_1 m(P)$ in the region of coexistence of $A$ and $M$ ($P < 2$) for both potentials are presented in Fig. 6. We also define $\xi_{61}$, $\xi_{62}$, $\xi_{41}$, and $\xi_{42}$:

$$g_6 = \xi_{61}^3 (\xi_{62}^2 - \xi_{61}^2) (\xi_{61}^2 - \xi_{62}^2), \quad \xi_{61} = \sqrt{0.5(1 - \sqrt{1 - 4B_6})},$$

$$\xi_{62} = \sqrt{0.5(1 + \sqrt{1 - 4B_6})};$$

(48)

$$g_4 = \xi_{41}^3 (\xi_{42}^2 - \xi_{41}^2) (\xi_{41}^2 - \xi_{42}^2), \quad \xi_{41} = 0.5(1 - \sqrt{1 - 4B_4}),$$

$$\xi_{42} = 0.5(1 + \sqrt{1 - 4B_4}).$$
We will analyze all results in terms of $P$, because it is the same for both polynomials, and in terms of $0 \leq B_4 \leq 9/32$ and $0 \leq B_6 \leq 1/3$, which vary over narrow ranges and allow more vivid comparisons. It is also convenient to use the parameter $\alpha := P/(4 - P)$: $\alpha = 0$ for thermodynamic equilibrium, $\alpha = 1$ when $\mathcal{M}$ loses its stability, and $\alpha = -1$ when $\mathcal{A}$ loses its stability. Dimensionless order parameters and potentials are convenient for intermediate steps in calculations but our solutions of the time-independent Ginzburg-Landau equations are always presented in terms of the physical parameter $\eta(x)$ for two reasons: first, there is no direct scaling between $\varphi(\xi)$ and $\varphi(\eta)$, and second, the dimensionless parameters for the two potentials—$k_4$ and $k_6$, for example—differ significantly for the same thermodynamic state.

Equilibrium and PT lines in the $s_1$-$s_2$ plane are shown in Fig. 7. The line $s_2 = 0$ ($P = 0$ and $B_4 = B_6 = 1/4$) is the equilibrium line between $\mathcal{A}$ and $\mathcal{M}$. For $s_2 > 0$ ($P > 0$ and $B > 1/4$) and $s_1 > 0$, $\mathcal{A}$ is stable (relative to $\mathcal{M}$), and for $s_2 < 0$ ($P < 0$ and $B < 1/4$) and $s_1 > 0$, $\mathcal{M}$ is stable. Martensite is also stable (relative to $\mathcal{A}$) for $s_1 < 0$ and $P > 0$. The line $s_1 = 0$ for $s_2 < 0$ ($P = -\infty$ and $B = 0$) is the line of loss of stability of $\mathcal{A}$; i.e., for $s_1 < 0$ and $s_2 < 0$ ($P > 0$), only $\mathcal{M}$ can exist, though not everywhere in this region. The line $P = 2$ ($B_4 = 9/32$, $B_6 = 1/3$) for $s_1 > 0$ is the line of loss of stability of $\mathcal{M}$; i.e., for $P > 2$ and $s_1 > 0$, only $\mathcal{M}$ can exist. Consequently, both phases coexist in the sector $-\infty < P < 2$ ($0 < B_4 < 9/32$, $0 < B_6 < 1/3$) for $s_1 > 0$. The sector $-\infty < P < 2$ ($0 < B_4 < 9/32$, $0 < B_6 < 1/3$) for $s_1 < 0$ is an unphysical region because both $\mathcal{M}$ and $\mathcal{A}$ are unstable. In fact our potentials were designed to describe material behavior in the coexistence region and at instability lines. Our potentials are not applicable outside this region. Some of the above inequalities cannot be expressed in terms of $B$ because $B$ is a nonmonotonic function of $P$.

Austenite is stable relative to $\mathcal{M}$ in the wedge $s_1 > 0$, $P > 2$, but for $P > P_c$, where $P_{6c}^A = 8/3$ and $P_{4c}^A = 3$, there is an artificial minimum more stable than $\mathcal{A}$ at $\eta > 1$ [see Eq. (43)]. For $s_1 < 0$ and $P > 2$, $\mathcal{M}$ is stable relative to $\mathcal{A}$, but for $2 < P < P_c$, where $P_{6c}^M = 3$ and $P_{4c}^M = 4$, a finite barrier at $\eta > 1$ separates the martensitic minimum from an infinitely deep potential well. For $s_1 < 0$ and $P < 2$, where $\mathcal{A}$ and $\mathcal{M}$ are unstable, there is an artificial minimum at $0 < \eta_1 < 1$.

These drawbacks do not affect the properties of the system in the coexistence region or along instability (PT) lines, but problems can arise when thermomechanical loading moves the point $(s_1, s_2)$ too close to the unphysical wedge in the $s_1$-$s_2$ plane. If the initial phase is metastable, then rapid loading toward the unphysical wedge can result in a transformation to a spurious phase. On the other hand, if the rate of thermomechanical loading is sufficiently low, then the transition will be into the stable phase. In general, however, the rate will not be low enough to ensure transformation to the stable phase, but even if this is the case or if the initial phase is stable, the point $(s_1, s_2)$ must not move too close to the unphysical wedge or else the small potential barrier separating the stable phase from the spurious phase will be surmounted by thermal fluctuations. These shortcomings in the potentials can be circumvented by modifying them outside the region of phase coexistence. The only requirements for such a modification are that it be continuous on the instability lines and that it have only one minimum in the region of $\mathcal{M}$ instability at $\eta = 0$ and a single minimum in the region of $\mathcal{A}$ instability at $\eta = 1$. So, for example, for $P > 2$ we can put

$$
\tilde{G}_6 = s_1 \eta^2(P - 1 - \eta^2 + \eta^4/3)/2,
$$

$$
\tilde{G}_4 = s_1 \eta^2 [P - 1 - (4/3) \eta + \eta^2/2], \quad s_1 > 0;
$$

$$
\tilde{G}_6 = s_1 (1 - s_1) P \eta^4 (\eta^2/3 - 1/2)/2,
$$

$$
\tilde{G}_4 = s_1 (1 - s_1) P \eta^2 (\eta^1/3 - \eta^4/4), \quad s_1 < 0.
$$

With such a modification, regions where only one phase exists can be correctly described in terms of $P$ and $B$. For $P > 2$ ($0 < B_4 < 9/32$, $0 < B_6 < 1/3$), only $\mathcal{A}$ exists for $s_1 > 0$ and only $\mathcal{M}$ exists for $s_1 < 0$.

As an alternative to modifying the potential, the order parameters can be constrained in numerical simulations to the interval $0, 1$ in the case of the extended 2-4-6 potential. In other words, reflective boundary conditions can be imposed at the ends of these intervals.

Introducing new spatial and time variables by the equations

$$
y_6 = \frac{k_6}{\sqrt{\beta m_6}} x = \sqrt{s_1} \frac{1}{2 \beta B_6} x = \sqrt{\beta} \frac{\sqrt{6}}{4} \sqrt{s_1} \frac{4 - P}{\beta \sqrt{3} - P} x, \quad z_6 = \frac{\lambda k_6^2}{m_6} t;
$$

$$
y_4 = \frac{k_4}{\sqrt{\beta m_4}} x = \sqrt{s_1} \frac{1}{\beta B_4} x = \frac{2}{3} \sqrt{s_1} \frac{1}{\beta} \frac{6 - P}{\sqrt{4} - P} x, \quad z_4 = \frac{\lambda k_4^2}{m_4} t,
$$

we obtain the dimensionless form of the Ginzburg-Landau equation

$$
\frac{\partial \xi}{\partial z} = - \left( \frac{\partial G}{\partial \xi} - 2 \frac{\partial^2 \xi}{\partial y^2} \right).
$$

Henceforth we consider only time independent solutions—i.e., $\partial \xi/\partial z = 0$. The resulting equation $2d^2\xi/dy^2 = dg/d\xi$ is
the equation of motion of a material point with mass equal to 2 in the potential field \(-g(\xi)\). An energy integral reads
\[
d\xi/dy = \sqrt{g - g_0},
\]
(52)
where \(g_0\) is the integration constant. At points where
\(d\xi/dy = 0\), e.g., at the center of a nucleus, \(g = g_0\). Designating
\[
g_{GL}^* = g_{GL} - g_0 = g - g_0 + (d\xi/dy)^2
\]
and taking into account Eq. (52), one finds that the contributions to \(g_{GL}^*\) from \(g - g_0\) and the gradient of the order parameter \(\xi\) are the same, hence \(g_{GL}^* = 2(g - g_0)\). Generally, Eq. (52) has periodic solutions with \(n\) diffuse interfaces. The total energy per unit area of \(n\) diffuse interfaces is given by
\[
e = \int_{-l}^{l} g_{GL}^* dy = 2n \int \sqrt{g - g_0} d\xi,
\]
where \(l = \sqrt{s_1/|\beta B|} L\), \(2L\) is the length of a parallelepiped in the \(x\) direction, and the integration limits of the second integral depend on the type of interface. The energy \(e\) is finite even for an infinite slab. The total energy of the system is infinite for an infinite parallelepiped in the case \(g_0 \neq 0\).

Falk\(^5\) found periodic solutions for \(n\) domain walls in finite regions, but claims that the separation between domain walls must be infinite in an infinite region. However, all of his finite-\(l\) solutions depend on \(l\) only through the combination \(l/n\). Consequently, the finite-\(l\) solutions can be used for \(l \to \infty\) provided \(n \to \infty\), keeping the ratio \(l/n\), the distance between the domain walls, finite.

Imposing the usual boundary conditions at the ends of the slab
\[
d\xi(-l)/dy = d\xi(l)/dy = 0,
\]
one obtains
\[
g(-l) = g(l) = g_0.
\]
(56)
Using Eq. (45), one derives
\[
y_4(\xi_4) = \int \frac{d\xi_4}{\sqrt{B_4 \xi_4^2 - \xi_4 + \xi_4 - 840}},
\]
\[
y_6(\xi_6) = \int \frac{d\xi_6}{\sqrt{B_6 \xi_6^2 - \xi_6 + \xi_6 - 860}}.
\]
(57)
Despite the significant differences between our theory and Falk’s\(^5\) and completely different variables and parameters, Eq. (57) is of the same form as Eq. (14) in Ref. 5. This means that we can use all of Falk’s formal periodic analytical solutions and analyze them in terms of our governing parameters for the 2-4-6 potential. The same procedure can be followed for the calculation of the total energy of the system.

\section*{B. Critical martensitic nucleus: \(M\) soliton in \(A\)}

Let us start with the case when \(A\) exists as \(x \to \pm \infty\), hence \(g_0 = 0\). The solutions below are valid in the region of stability of \(M\) and metastability of \(A\), i.e., \(s_1 > 0\) and \(P \approx 0\) (0 \(\leq B \leq 1/4\)). One has

\[
\xi_{41}^M(y_4) = \frac{\xi_{41}}{1 + (1 - \frac{\xi_{41}}{\xi_{42}}) \sinh^2[\sqrt{B_4(y_4 - y_{04})}/2]}
\]
\[
\xi_{61}^M(y_6) = \frac{\xi_{61}}{\sqrt{1 + (1 - \frac{\xi_{61}}{\xi_{62}}) \sinh^2[\sqrt{B_6(y_6 - y_{06})}]}}
\]
\[
\eta_4^M(x) = \frac{\xi_{41}}{k_4} \left( \frac{s_1}{2 \beta B_4} \right)^{x/4}
\]
\[
\eta_6^M(x) = \frac{\xi_0}{k_6} \left( \frac{s_1}{2 \beta B_6} \right)^{x/4}
\]
\[
e_4^M = (3 - 8B_4) \sqrt{B_4}/6 + (B_4 - 1/4) \ln \frac{1 + 2 \sqrt{B_4}}{1 - 4B_4}
\]
\[
e_6^M = \sqrt{B_6}/2 + (B_6 - 1/4) \ln \frac{1 + 2 \sqrt{B_6}}{1 - 4B_6}
\]
\[
E_4^M = \frac{1}{k_4^2} \sqrt{B_4 / 2 B_4 c_4^M} = \frac{32}{27} (6 - P)^3 \sqrt{\beta s_1 e_4^M}
\]
\[
E_6^M = \frac{1}{k_6^2} \sqrt{B_6 / 2 B_6 c_6^M} = \frac{3 \sqrt{6}}{8} \left( \frac{4 - P}{3 - P} \right)^{1/2} \sqrt{\beta s_1 e_6^M}
\]

The solution \(\xi_{61}^M(y_6)\) formally coincides with Falk’s solution.\(^5\) Falk did not provide a physical interpretation of his solution, but we do so here. At first sight, the solution (58) looks contradictory: the smaller \(P\) (more negative \(P\)) and the greater the stability of \(M\), the smaller the magnitude of the order parameter of the \(M\) nucleus. This apparent contradiction disappears if we interpret the above solution as a critical martensitic nucleus in austenite. We verified by numerically solving the Ginzburg-Landau equation (51) that this solution corresponds to unstable thermodynamic equilibrium. An initial profile slightly larger (or smaller) than
(a) Growth of a supercritical $M$ nucleus ($B = 0.2$, $w = 1.1$). (b) Disappearance of a subcritical $M$ nucleus ($B = 0.24$, $w = 0.9$). (c) Growth of a supercritical $A$ nucleus ($B = 0.3$, $w = 1.1$). (d) Disappearance of a subcritical $A$ nucleus ($B = 0.26$, $w = 0.9$). All plots are for the 2-4-6 potential.

Consider a supercritical nucleus, i.e., $w > 1$, for which we expect $\partial \xi / \partial z > 0$. However, this is true only when $\xi_{s, \text{max}}$ satisfies $\xi_{s, \text{max}}^2 < 2(3(1 + w^2)] < 1/3$, which is the case for $B < 2/9$. For a small thermodynamic driving force $2/9 < B \leq 1/4$, the inequality $\xi_{s, \text{max}}^2 < 2(3(1 + w^2)]$ is violated in the central part of the nucleus. Consequently, the magnitude of $\xi$ initially decreases near the center of the nucleus while it grows in the rest of the nucleus. After a short initial stage, growth occurs throughout the nucleus.
For a subcritical nucleus, $w < 1$. $\partial \xi / \partial z < 0$ if the same inequality is satisfied. In this case, the central region of the nucleus grows during a brief initial stage, after which $\xi$ decreases throughout the nucleus until it disappears.

The above analytical estimates provide important insights into the behavior of the nuclei but, of course, detailed, quantitative results on the growth or shrinkage of the nuclei can only be obtained from numerical simulations, for example, Fig. 8.

As was mentioned, for the 2-4-6 potential we can use Falk’s periodic, multinuclei solutions for a finite region the energy of such solutions (the activation energy for nucleation) is roughly proportional to the number of nuclei $n/2$. However, the physical interpretation of multinuclei solutions is unclear. Is this a stable solution or an unstable one? If it is a metastable configuration, can it be reached under some dynamic process and how high is the energy barrier that separates it from a lower-energy state with a smaller number of nuclei or from a complete M state? These problems will be studied elsewhere.

The amplitudes of the physical order parameters of the critical M nuclei are

$$
\eta_{41} = \frac{\xi_{41}}{k_4} = \frac{4(1 - \sqrt{1 - 4B_4})}{3 + \sqrt{9 - 32B_4}},
$$

$$
\eta_{61} = \frac{\xi_{61}}{k_6} = \frac{3 - \sqrt{1 - 4B_6}}{2 + \sqrt{1 - 3B_6}}.
$$

From now on, a subscript “1” on an order parameter will indicate the amplitude of that order parameter. The functions $\eta_1$ and $\varphi(\eta_1)$ vs $B$ are shown in Fig. 9. The amplitude $\eta_{61}$ is significantly larger than $\eta_{41}$ except at the end points $B = 0$ and $B = 1/4$. Note that $d \eta_1 / dB$ is infinite at the end points for the 2-4-6 potential and only at $B = 1/4$ for the 2-3-4 polynomial.

Figure 10 shows $E^M/\sqrt{\beta s_1}$ as a function of $\alpha = P/(4 - P)$. The energy of the 2-3-4 critical M nucleus is smaller than the energy of the critical M nucleus for the 2-4-6 potential. The activation energy in thermodynamic equilibrium ($\alpha = 0$) is finite, in contrast to the infinite energy of a classical nucleus with a sharp interface. When $A$ loses its stability, $E^M_0 = E^M = 0$, while the activation energy is finite in classical nucleation theory.

The profiles $\eta(\sqrt{s_1/\beta x}, P)$ and $\varphi(\sqrt{s_1/\beta x}, P)$ of the critical nuclei are shown in Fig. 11 for various $P$ and $B$. The $\varphi$ profiles are essentially strain profiles because $\varepsilon(\eta(x))$ is the transformation strain. The $\varphi$ and $\eta$ profiles are quite different, especially for small $\eta$ and $1 - \eta$ where the strongest nonlinearities of the function $\varphi$ are located. The $\varphi$ profiles are narrower than the $\eta$ profiles. For $P = -1$ the 2-4-6 and 2-3-4 nuclei are almost indistinguishable. At larger $P$ the 2-4-6 and 2-3-4 nuclei have the same amplitudes but the 2-3-4 nucleus is wider. At smaller $P$, $\varphi_6[\eta_6(x)]$ is significantly greater than $\varphi_4[\eta_4(x)]$ everywhere. When $P \to 0$, the entire region is martensite.

The effective width $W$ of the nucleus can be defined as $W = 2u(\infty)/\varepsilon(\eta_1)$, where $u(\infty)$ is the displacement at infinity and $\varepsilon$ is the volumetric strain. Thus a nucleus of width $W$ with a sharp interface and constant volumetric strain $\varepsilon(\eta_1)$ produces the same displacement increment as the critical nucleus. The displacement at infinity due to volumetric strain can be calculated by integrating

$$
\varepsilon(\eta(x)) = \frac{du}{dx},
$$

where $u(0) = 0$. The total displacement contains an additional contribution due to constant elastic strain, $u_0 = 2l\text{Im} x; \alpha$, which we neglect here. The effective widths of the nuclei are
where $x_m$ corresponds to the maximum of the derivative $d\eta(x)/dx$. The ideal definition would be $\Delta^M := \phi(\eta_1)/|d\phi[\eta(x)]/dx|_{max}$, but this cannot be analyzed analytically. The interface thicknesses are

$$\Delta_4^M = \frac{(3 + I_4)^5[12B_4 - (I_4 - 3)(J_4 - 1)]}{96\sqrt{B_6}(1 + I_4)(1 + I_6 + 2J_6)^2[3(3 + I_4) - 32B_4]\sqrt{(I_4 - 3)(1 + J_4) + 12B_4}} \sqrt{\beta/s_1},$$

$$\Delta_6^M = \frac{(1 + J_6)^4[4B_6 - (I_6 - 1)(J_6 - 1)]}{2\sqrt{B_6}(1 + I_6)(1 + I_6 + 2J_6)(1 + J_6 - 3B_6)\sqrt{(1 + I_6)(J_6 - 1) + 4B_6}} \sqrt{\beta/s_1},$$

$$I_4 := \sqrt{9 - 32B_4}, \quad J_4 := \sqrt{1 - 4B_4}, \quad I_6 := \sqrt{1 - 4B_6}, \quad J_6 := \sqrt{1 - 3B_6}.$$

The dimensionless width $W^M_{\sqrt{s_1}/\beta}$ and dimensionless thickness $\Delta^M_{\sqrt{s_1}/\beta}$ are plotted as functions of $B$ in Fig. 12. The width $W^M_{\sqrt{s_1}/\beta}$ tends to infinity for both potentials as the PT equilibrium line ($B = 1/4, P = 0$) is approached, while the interface thickness $\Delta^M_{\sqrt{s_1}/\beta}$ remains finite. As $B \rightarrow 0$ ($s_1 \rightarrow 0$), $W^M_{\sqrt{s_1}/\beta}$ and $\Delta^M_{\sqrt{s_1}/\beta}$ go to finite values; therefore, $W^M$ and $\Delta^M$ tend to infinity. Excluding the neighborhood of $B = 1/4$, both parameters are of comparable magnitude; the interface is sharp only near thermodynamic equilibrium. The width of the nucleus is larger for the 2-4-6
potential than for the 2-3-4 potential. The interface thickness is significantly larger for the 2-3-4 potential for \( B > 0.17 \) and almost the same for both potentials for smaller \( B \).

The interface thicknesses \( \Delta_4^M \) and \( \Delta_6^M \) are given to within 0.4% by the cubic polynomial approximations

\[
\Delta_4^M = (1.942 + 1.779B_4 - 12.80B_4^2 + 68.56B_4^3) \sqrt{\frac{\beta}{s_4}},
\]

\[
\Delta_6^M = (2.000 + 0.732B_6 + 0.381B_6^2 + 10.66B_6^3) \sqrt{\frac{\beta}{s_6}}.
\]

The effective surface energy of a nucleus is defined in Ref. 7 as \( \Gamma^M := [E^M - G(\eta_1)W]/2 \), so \( G(\eta_1)W \) is the bulk energy of the nucleus. However, \( G(\eta_1) = 0 \) by definition of \( \eta_1 \) [see Eq. (52) for \( d\xi/dy = 0 \) and \( g_0 = 0 \)]; i.e., the energy of the nucleus is localized at its surface according to this definition. For our theory, a better definition is \( \Gamma^M := [E^M - G(\varphi(\eta_1))W]/2 \) since \( G(\varphi(\eta_1)) \neq 0 \).

C. Kink solutions: A-M diffuse interfaces

We consider the case where the phase is \( A \) as \( x \to -\infty \) and \( M \) as \( x \to +\infty \). Then, \( g(-\infty) = g(A) = g(0) = 0 \) and \( g(+\infty) = g(M) = g_0 \), i.e., \( g(A) = g(M) = 0 \), which is the case when \( A \) and \( M \) are in thermodynamic equilibrium: \( s_2 = P = 0 \), \( B = 1/4 \), \( \xi_{41} = \xi_{42} = \xi_{50}^2 = 1/2 \), \( g_6 = \xi_{62}^2(\xi_0^2 - 1/2)^2 \), \( g_4 = \xi_6^2(\xi_0^2 - 1/2)^2. \) The solutions of Eq. (52) read

\[
\xi_{4A}^M(y_4) = [2(1 + e^{-(y_4 - \gamma_0/2)})]^{-1},
\]

\[
\xi_{6A}^M(y_6) = [2(1 + e^{-(y_6 - \gamma_0/2)})]^{-1/2}, \quad \varepsilon_{6A}^M = 3\varepsilon_{4A}^M = 1/8;
\]

\[
\eta_{4A}^M(x) = \{1 + \exp[-\sqrt{s_4/\beta(x-x_0)}]\}^{-1},
\]

\[
\eta_{6A}^M(x) = \{1 + \exp[-\sqrt{2s_4/\beta(x-x_0)}]\}^{-1/2}.
\]

The solution \( \eta_{4A}^M(x) \) is symmetric around \( x = x_0 \) but \( \eta_{6A}^M \) is not (see Fig. 13) because the \( A \) and \( M \) minima of the 2-4-6 potential have different curvatures [note, however, that \( (\eta_{6A}^M)^2 \) is symmetric around \( x = x_0 \)]. In Fig. 13 we used \( x_{04} = 0 \) and \( x_{06} = -\ln 3 \) so that \( \eta_{6A}(0) = g_{4A}(0) = 1/2 \). The strain profiles \( \varphi_A(\eta(x)) \) and \( \varphi_M(\eta(x)) \) are very close and exhibit smaller interface thicknesses than the \( \eta(x) \) profiles.

\( A \) and \( M \) are in thermodynamic equilibrium, thus \( s_2 = P = 0 \), and consequently, \( \Delta G_A^M = \sigma_4 \varepsilon_A, B = 1/4, \) and \( k_0^M = 1/2 \). The interface energy densities are...
are accurately approximated by the polynomials

\[ E_6^{AM} = \frac{3}{4} \sqrt{2} E_4^{AM} = \frac{\sqrt{2} \beta s_1}{4} = \frac{\sqrt{2} \beta}{4} \sqrt{A - a^e_{0}}. \]

Both \( \Delta_4^{AM} \) and \( \Delta_6^{AM} \) are complicated functions of \( a \) but they are accurately approximated by the polynomials

\[ 2.411 \leq p_4 = -0.028(a - 3)^2 + 2.667 \leq 2.667. \]

The interface thicknesses are given by

\[ \Delta_6^{AM} = \frac{p_6}{p_4} \Delta_4^{AM} = p_6 \sqrt{\frac{\beta}{s_1}} = p_6 \sqrt{\frac{\beta}{A_0(\theta - \theta_c) - \Delta G^a a}} \]

\[ = \sqrt{\frac{\beta}{a(6 - a) \theta e_H}}. \]

\[ \Delta_6^{AM} = \frac{2}{3} \sqrt{\frac{\beta}{G_6(\eta_6)}}. \]

\[ \Delta_4^{AM} = \frac{p_4}{p_6} \sqrt{\frac{\beta}{G_4(\eta_4)}}. \]

where \( G_6(\eta_6) = 2s_1/27 \) and \( G_4(\eta_4) = s_1/16 \) are the energy barriers between \( A \) and \( M \) at thermodynamic equilibrium. Equation (69) expresses the A-M interface energy in terms of the material parameters and temperature (or stress, which is related to temperature via the equilibrium condition \( s_2 = 0 \)), the stress hysteresis, or the energy barrier between \( A \) and \( M \) at thermodynamic equilibrium.

The interface thickness is defined by

\[ \Delta_4^{AM} = \left( \frac{d \varphi[\eta(x)]}{dx} \right)_{max}, \]

which results in

\[ \Delta_4^{AM} = \frac{(21 - 5a + K_4)^5}{32(a - 6)^3[11a^3 - 81(9 + K_4) - 5a^2(24 + K_4) + a(48 + 39K_4)]} \sqrt{\frac{\beta}{s_1}}. \]

\[ \Delta_6^{AM} = \frac{(72 - 15a + K_6)^4}{128 \sqrt{2}(a - 6)^4[-27a^2 - 24(24 + K_6) + 5a(48 + K_6)]} \sqrt{\frac{\beta}{s_1}}, \]

\[ K_4 := \sqrt{81 - 30a + 5a^2}, \quad K_6 := \sqrt{576 - 240a + 33a^2}. \]

Both \( \Delta_4^{AM} \) and \( \Delta_6^{AM} \) are complicated functions of \( a \) but they are accurately approximated by the polynomials

\[ 1.88 \leq p_6 = 1.88 + 0.179a + 0.00065a^2 - 0.0035a^3 \leq 2.386, \]

\[ 2.411 \leq p_4 = -0.028(a - 3)^2 + 2.667 \leq 2.667. \]

The differences in the A-M interface profiles and energy densities between the 2-4-6 and 2-3-4 potentials are not significant.

D. Critical austenitic nuclei: A solitons on M

In this section we consider the case where only \( M \) exists as \( x \to \pm \infty \). The integration constant \( g_0 \) must be a function of the parameters \( k_6 \) or \( k_4 \) in order to satisfy the boundary conditions \( d \xi(\pm \infty)/dy = 0 \):

\[ g_4 - g_40 = (k_4 - \xi_4)(\xi_4 - \xi_{A1})(\xi_4 - \xi_{A2}), \]

\[ \xi_{A1} = \frac{1}{2}(1 - 2k_4 + \sqrt{1 - 2k_4}) \geq 0, \]

\[ \xi_{A2} = \frac{1}{2}(1 - 2k_4 - \sqrt{1 - 2k_4}) \leq 0, \]

\[ g_6 - g_60 = (k_6^2 - \xi_6^2)(\xi_6^2 - \xi_{A}^2), \quad \xi_{A} = \sqrt{1 - 2k_6^2}. \]

The solutions of Eq. (52) are...
The parameters \( k_6 \) and \( k_4 \) are restricted to the intervals \([1/\sqrt{3}, 1/\sqrt{2}]\) and \([3/8, 1/2]\), respectively. It was proved numerically (as was done for the martensitic nucleus) that the solutions \( \xi_6(y_6) \) and \( \xi_4(y_4) \) describe critical austenitic nuclei (see Fig. 8). From Eq. (76) we obtain the physical order parameters as functions of \( P \):

\[
\eta_6(x) = \frac{\sqrt{P}}{\sqrt{2(3-P) - 3(2-P) \tanh^2 \left( \frac{1}{2} \sqrt{\frac{s_1}{\beta}} x \right)}}.
\]

\[
\eta_4(x) = 1 - \frac{6(2-P)}{4(3-P) + \sqrt{2P(6-P)} \cosh \left( \sqrt{\frac{s_1}{2\beta}} (2-P)x \right)}.
\]
where $0 \leq P \leq 2$. The total energies per unit area of the critical nuclei are

$$E^A_4 = \frac{32}{27} \sqrt{\beta s_1} \frac{(6-P)^3}{(4-P)^{5/2}} e^A_4,$$

$$e^A_4 = 4 \int_{\xi_1}^{\xi_4} \left( \frac{3}{2} \frac{(12-6P+P^2)}{(2P)(4-P)(2-P)} - P(3-P)(6-P) \ln \left( \frac{4(3-P) + 3\sqrt{2(4-P)(2-P)}}{\sqrt{2P(6-P)}} \right) \right) d\xi_4$$

$$= \frac{1}{4(6-P)^3} \left[ \frac{3}{2} \frac{(12-6P+P^2)}{2\sqrt{(4-P)(2-P)}} \right]$$

$$- P(3-P)(6-P) \ln \left( \frac{4(3-P) + 3\sqrt{2(4-P)(2-P)}}{\sqrt{2P(6-P)}} \right)$$

$$= 0.083 - 0.086P + 0.024P^2 - 0.001P^3;$$

$$E^A_b = \frac{3}{8} \sqrt{\beta s_1} \frac{(4-P)^2}{(3-P)^{3/2}} e^A_6.$$

As was done for the martensitic nucleus, expressions for the width and interface thickness can be obtained for the austenitic nucleus.

Figure 10 shows the energies of the critical $A$ nuclei for the 2-4-6 and 2-3-4 potentials versus $\alpha$, and Fig. 14 shows profiles of the critical $A$ nuclei for these two potentials. The results for the two potentials are very similar except for the widths in the neighborhood of $P = 0$ where the 2-3-4 nucleus is significantly narrower than the 2-4-6 nucleus.

E. Kink solutions: M-M interfaces and barrierless nucleation of austenite

In this section we present two M-M kink solutions of the static Ginzburg-Landau equations. The first is a solution for the potentials in hyperspherical coordinates, and the second is a $M_+\cdot M_-$ solution of the extended ($\eta \in [-1,1]$) 2-4-6 Landau potential that exhibits barrierless nucleation of austenite.

The minimum-energy paths between stable martensitic variants for the potentials in hyperspherical coordinates are great circles on the unit hypersphere, $r = 1$. Kink solutions among martensitic variants exist when both variants have the same energy, which implies zero stress or zero transformation work. The potential along the great circle from $M_1$ to any other variant is $G = A \psi^2 (1 - \psi^2) + \Delta G^A$ for both potentials. Both variants are twin-related IPS variants, $\epsilon_4(\psi) = \frac{1}{2} \gamma_4 (-1 + 2 \psi^2 (3 - 2\psi)) [m'm + mn'n] + nn'n$ [see Eqs. (20) and (27)]; that is, the normal strain is constant, the shear strain varies from $-\gamma_1$, $\gamma_2$, and the PT does not proceed through $A$. The solution of the static Ginzburg-Landau equation $\partial G/\partial \psi = 2\beta \partial^2 \psi/\partial x^2$ is

$$\psi = (1 + \exp[-\sqrt{A}/\beta(x-x_0)])^{-1},$$

which interpolates between $M_1$ at $-\infty$ and $M_{1+a}$ at $+\infty$. The solution (79) coincides with Eq. (68) for $\eta^AM$ when $s_1$ is substituted for $A$. For $a = 3$, $P(\psi) = \varphi_4(\psi)$; thus the thickness of the interface is given by Eqs. (72) and (73) for $\Delta^AM$ with $s_1 \rightarrow A$: $\Delta^AM = 2.667 \sqrt{\beta/3}$. The total kink energy per unit area is $E^MM_b = \sqrt{\beta/3}$.

The static Ginzburg-Landau equation for the 2-4-6 potential admits a kink solution such that $\eta^+(+\infty) = +1$, $\eta^-(+\infty) = -1$; i.e., the structure goes to $M_+$ as $x \to +\infty$ and to $M_-$ as $x \to -\infty$. There is no corresponding solution for the 2-3-4 potential, so we can drop the subscript "6." Equation (75)
This solution is valid for $P \ll 0$, $0 \ll B \ll 1/4$. Since $s_1e_i = 0$, it follows that $P = 12\Delta G^\theta/A$; hence $\Delta G^\theta \ll 0$ since $P \ll 0$, which implies stability of $M$ and metastability of $A$, or equilibrium. The profiles $\eta(x)$ and $\varphi[\eta(x)]$ for various $P$ are shown in Fig. 15. The total energy per unit area of the $M_s$-$M_e$ interface is

$$E_{MM} = \frac{1}{k^2} \frac{\beta s_1}{2B} e^{\varepsilon_{MM}}.$$

(82)

$$e^{MM} = 4 \int_0^\varepsilon (k^2 - \xi^2) \sqrt{\xi^2 + \xi_A^2} d\xi$$

$$= \frac{1}{2} \left[ k \sqrt{3k^2 - 1} + (1 - 8k^2 + 12k^4) \ln \left( \frac{k + \sqrt{3k^2 - 1}}{\sqrt{2k^2 - 1}} \right) \right].$$

Figure 10 shows $E_{MM}/\sqrt{\beta s_1}$ versus $\alpha$. Note that $E_{MM}/\sqrt{\beta s_1} \to \infty$ when $B \to 0$ ($a \to -1$); however, $s_1/B = 3s_2/4$ and $E_{MM}/\sqrt{\beta} \to 0.901 \sqrt{\beta} = 3.12 \sqrt{\Delta G^\theta}$ in the same limit. When $P \to 0$, $E_{MM}/\sqrt{\beta} \to \sqrt{s_1/2} = \sqrt{\Delta T^2}$. The energy of the $M_s$-$M_e$ interface and the energies of the critical $A$ and $M$ nuclei all coincide when $A$ and $M$ are in thermodynamic equilibrium.

It is convenient to introduce the dimensionless temperature $T := (\theta_e - \theta)/(\theta_e - \theta_m)$, $0 \leq T \leq 1$. Then $s_1 = A = A_0(\theta_e - \theta_m)(1 - T)$ and $P = 12r T[A_0(T - 1)]$. Plots of $E_{MM}/\sqrt{\beta A_0(\theta_e - \theta_m)}$ vs $T$ for various values of $0 \ll A_0/12z \ll 1/2$ are shown in Fig. 16.

As was mentioned in Ref. 11 and 12, soliton splitting occurs (Fig. 15) as the $A$-$M$ equilibrium line is approached ($B \to 1/4, P \to 0$); that is, the $M_s$-$M_e$ diffuse interface splits into $M_s$-$A$ and $A$-$M_e$ diffuse interfaces separated by an $A$.
As $P \to 0^-$ the solution (81) for $\eta(x)$ assumes the form $\text{sgn}(x)/(1 + 6[|P| \sin^2(\sqrt{8/\beta}x)])^{1/2}$, whose magnitude is less than or equal to $\delta$ for $|x| \leq x_\delta$, where $x_\delta = \sqrt{\beta/(2s_1 \ln(24\beta^2/|P|))}$ for $|P| \ll \delta < 1$; the width of the austenitic region grows logarithmically as the equilibrium line is neared.

The thickness of the $M_1$-$M_+$ interface can be estimated for $P \ll -1$ by the expression

$$D_{MM} = \frac{2x_{0.95}}{\sqrt{\beta A_0(\theta_c - \theta_\pm)}}.$$

Here $x_{0.95}$ is defined by the condition $\varphi[\eta(x_{0.95})] = 0.95$. Equation (83) was obtained from the condition $\varphi(x_{0.95}) = 0.95$ using Eq. (81) 2. The function $\eta_{0.95}(a)$ was determined by numerical solution of the equation $\varphi(\eta_{0.95}) = 0.95$ and then approximated by the cubic polynomial, Eq. (83) 2. Plots of $\Delta_{MM, \eta} \sqrt{8/\beta}$ vs $B$ for various $a$ and $\Delta_{MM, \eta} \sqrt{A_0(\theta_c - \theta_\pm)/\beta}$ vs $T$ for $a = 2.98$ (NiAl value) and various values of $0 \leq A_0/12z \leq 1/2$ are shown in Fig. 17. For $P \gg -1$ the splitting is so pronounced that we no longer have an interface in the usual sense of the word. Equation (83) then gives the width of the austenitic nucleus.

Near the $A$-$M$ equilibrium line, $0 < k^2 - 1/2 \ll 1$, and Eq. (81) for the order parameter becomes
\[ \xi(y) = \sqrt{2} \sinh(y/2) \left[ \exp(y_0) + 4 \sinh^2(y/2) \right]^{-1/2}, \]
\[ y_0 = -\ln(k^2 - 1/2). \] (84)

Now expand the hyperbolic sine around \( y_0 \approx 1 \), \( \sinh(y/2) \approx \exp(y_0/2) \exp[(y-y_0)/2] \), and substitute into Eq. (84):
\[ \xi(y) = \left[ 2 \left( 1 + e^{-(y-y_0)} \right) \right]^{-1/2}. \] (85)

This is identical to \( \varepsilon_{\text{AM}}^{\text{M}} \) [see Eq. (68)], the A-M diffuse interface, as expected.

Austenite nucleation inside a stable martensitic phase is suppressed by the large activation energy [see Eq. (78)] required to form an unstable critical nucleus. In contrast, the formation of an A region between the M_\text{A} and M_\text{M} occurs with no cost in energy. Soliton splitting is a barrierless mechanism for A nucleation in the region of M stability. A stable austenitic nucleus is formed and grows as the temperature approaches the equilibrium temperature, and expands to infinity at the equilibrium temperature. Note that for \( P \ll 0 \), when the A embryo is not visible in the \( \eta(x) \) profile in Fig. 15, it can be seen in the \( \varphi(x) \) profile; this is because \( d \eta(0)/dx \neq 0 \) but \( d \varphi(\eta(0))/dx = [d \varphi(0)/d \eta(d \eta(0)/dx)] = 0 \). We believe that such a mechanism may be observable in experiments on three-dimensional systems when the transformation strain is an IPS (to avoid distortion along the interface). This may be the case for the interface between two IPS variants for any PT.

VI. NiAl CUBIC- TETRAGONAL PT: M-M AND M-A INTERFACES

Let us estimate the parameter \( \beta \) for NiAl alloys. The transformation strain for a variant-variant transformation in NiAl is an IPS and the transformation does not pass through A, so our results for M-M interfaces in polar coordinates are applicable to NiAl. Taking \( A = 5320 \) MPa [Eq. (39)] one obtains
\[ E_{\text{MM}}^\theta = 2.43 \times 10^4 \sqrt{\beta} N^{1/2} \text{m}^{-1}, \]
\[ \Delta_{\text{MM}}^\theta = 6.22 \times 10^{-5} \sqrt{\beta} N^{1/2} \text{m}. \] (86)

High-resolution electron microscopy\(^{13}\) of Ni_{63}Al_{15} (the data that we used in Ref. 2 and in Sec. IV are for Ni_{65}Al_{35}) brackets the width of the martensite-martensite interface between one and several interatomic distances (see Figs. 5 and 6 in Ref. 13). If we assume \( \Delta_{\text{MM}}^\theta = 0.3 \times 10^{-9} \) m, which corresponds to an interatomic distance, then we obtain \( \beta = 2.33 \times 10^{-11} \) N and \( E_{\text{MM}}^\theta = 0.117 \) J m\(^{-2}\) from Eq. (86). This value for \( \beta \) gives \( \Delta_{\text{MM}}^\theta = 0.243 \times 10^{-9} \) m from Eq. (73) and \( E_{\text{MM}}^\theta = 0.079 \) J m\(^{-2}\) from Eq. (74) for the stress-free case at \( \theta = 300 \) K. If we take \( \Delta_{\text{MM}}^\theta = 10^{-9} \) m, then \( \beta = 2.588 \times 10^{-10} \) N, \( E_{\text{MM}}^\theta = 0.391 \) J m\(^{-2}\), \( \Delta_{\text{MM}}^\theta = 0.809 \times 10^{-9} \) m, and \( E_{\text{MM}}^\theta = 0.263 \) J m\(^{-2}\) from Eq. (74). If the surface energy is known, then a more precise estimate of \( \beta \) can be made using Eq. (86) or Eqs. (73) and (74).

Note that the relatively high value of \( E_{\text{MM}}^\theta \) in comparison to 0.01-0.02 J m\(^{-2}\) for steels is related to the very high barriers for stress-induced PT, i.e., \( A_0 \theta (\theta_0 - \theta) \). Our Eq. (69) for \( E_{\text{MM}}^\theta \) in terms of \( \bar{G}_M (\eta_M) \), the energy barrier between A and M at thermodynamic equilibrium, exactly coincides with the corresponding equation in Ref. 7 because Eq. (69) is independent of stress, and at zero stress and for one M variant both Gibbs potentials coincide. Our value for \( A_\text{AM}^{\text{M}} \) at \( \alpha = 2.98 \) is 0.667 of the corresponding value in Ref. 7.

VII. PHASE FIELD THEORY OF DISLOCATIONS

In this section we discuss a serious shortcoming of the present-day phase field theory of dislocations and then demonstrate that this drawback can be eliminated by following an approach similar to the one we used to construct our Landau potentials.

In the phase field theory of dislocations (see, e.g., Ref. 3) the Burgers vector and consequently the plastic strain depend on the applied stress even in the elastic regime—that is, when dislocations are in stable equilibrium and no plastic flow occurs. Such a dependence is in conflict with the definition of plastic strain in macroscopic plasticity theory. A \( \sigma \)-dependent Burgers vector is inconsistent with the well-established theory of dislocations.\(^{14}\) It also implies dissipation during elastic deformation of plastically deformed material.\(^{10}\) The \( \sigma \) dependence of the plastic strain in the phase field theory is analogous to the \( \sigma \) dependence of the transformation strain in Landau theories of PT’s; see analysis in Ref. 1.

Consider one slip plane and one slip direction—i.e., one Burgers vector \( b \). Then Eqs. (3) and (4) in Ref. 3 for the Burgers vector and plastic strain reduce to \( b(\eta) = b\eta \) and \( \varepsilon_p(\eta) = b n \eta / d = e_p(\eta) \), where \( \eta \) is the density function (phase field) for dislocations, \( n \) is the normal to the slip plane, and \( d \) is the distance between the slip planes. The local potential of the crystal lattice [Eq. (8) in Ref. 3] is \( f = A \sin^2(\pi \eta) \), which leads to the Gibbs potential \( G = -\sigma \cdot \cdot \cdot - 2 \sigma \cdot e_p(\eta) A + \beta \sin^2(\pi \eta) \), the corresponding equation of thermodynamic equilibrium is \( \partial G / \partial \eta = 0 = -\sigma \cdot e_p + \pi A \sin(2\pi \eta) \delta \pi \eta \), or \( \varepsilon_p = \arcsin[\sigma / (\pi A)] + n \), where \( n = 0, 1, 2, \ldots \) is the number of dislocations. Therefore, in thermodynamic equilibrium, the order parameter \( \eta \), the Burgers vector \( b(\eta) \), and plastic strain \( \varepsilon_p(\eta) \) depend on the stress \( \sigma \). We can avoid this unphysical dependence on \( \sigma \) by first breaking the order parameter into an integer part \( \text{Int}(\eta) \) and a fractional part \( \tilde{\eta} = \eta - \text{Int}(\eta) \in [0,1] \), and then incorporating the dependence on \( \tilde{\eta} \) through the 2-3-4 or 2-4-6 polynomials \( \varphi(\eta) \), as was done for the transformation strain in our Landau potentials:
\[ b(\eta) = b[\varphi(\tilde{\eta}) + \text{Int}(\eta)], \quad \varepsilon_p(\eta) = b n [\varphi(\tilde{\eta}) + \text{Int}(\eta)] / d. \] (87)

The term \( \text{Int}(\eta) = n \) accounts for the presence of \( n \) dislocations in the slip plane, each with Burgers vector \( b \). The Gibbs potential for three shear stresses is shown in Fig. 18. The thermodynamic equilibrium condition \( \partial G / \partial \eta = 0 \) has the
The free surface boundary condition \( d\eta/dx = 0 \) is satisfied at the maxima of the \( A \) and \( M \) critical nuclei. Consequently, a critical nucleus at a free surface is simply half of a critical nucleus in the bulk. Since the energy of a surface nucleus is half of the energy of the corresponding nucleus in bulk, the probability of its appearance is significantly higher.

We plan to obtain and compare analytical and numerical solutions of the time-dependent Ginzburg-Landau equations for the 2-3-4-5 and 2-4-6 potentials. We also plan to develop a generalization of our Landau theory for large strains and large material rotation, a very challenging problem. Such a generalization is essential for PT's with components of transformation strain exceeding 0.1 and for loadings that are accompanied by finite rotations of the crystal lattice.
ACKNOWLEDGMENTS

Support of Los Alamos National Laboratory for V.I.L. under consulting agreement No. C-8060 and for V.I.L. and D.W.L. under Contract No. 52844 is gratefully acknowledged. V.I.L. also acknowledges NSF support (Grant No. CMS-02011108) and D.W.L. also acknowledges support of the ME Department of Texas Tech University. We would like to thank Dr. D. Schryvers for providing and discussing his data on the thickness of the variant-variant interface in NiAl.

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