Multivariant Martensitic Phase Transformations Beyond Mean Field Theory

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Despite the ubiquity of applications of martensitic transformations such as shape memory alloys and transformation induced plasticity (TRIP) steels, and its conceptual importance to materials science, it is one of the least studied solid-state transformations with an accurate theoretical description remaining elusive. Specifically, all previous work on the topic treats the system as spatially homogeneous - effectively employing a mean field theory. In this paper, we evaluate the role of fluctuations around the saddle-point minimum, revealing an upper critical dimension equal to $d = 3$ and indicating the need to go beyond mean field theory for all practical martensite transformations. To this end, we perform an ϵ-expansion using perturbative renormalization group at second order around the tricritical point, highlighting the existence of a stable fixed point.

Introduction

Martensitic transformations are first order, diffusionless, displacive transformations which can be either thermally or stress-induced (symmetry breaking) [1, 2]. Since the transformation is diffusionless, the local composition during the transformation must stay the same, and rather is accommodated via a spontaneous change of the crystal structure [2]. The transformation is in general reconstructive, i.e. group-subgroup relations need not exist between the high temperature phase historically called 'austenite' and the low temperature phase variants called 'martensite' , differentiating it with the class of continuous ferroelastic transitions [3–5]. We note however that the example of an $O_h \Leftrightarrow D_{4h}$ transformation we investigate in the present work the product phases are indeed subgroups of the parent phase, albeit still first order [1].

A successful theory describing such transformations is thus required to exhibit the following characteristics: (i) two-phase equilibrium between austenite and any of the crystallographically equivalent martensitic variants, $A \Leftrightarrow M_i$; (ii) stress-induced transformations characteristic of temperature (i.e. existence of hysteresis); (iii) allowed transformations between different martensitic variants, $M_i \Leftrightarrow M_j$, leading to the experimentally observed twinned microstructures [1, 6–8].

Landau theory is a phenomenological framework based on symmetry considerations and analyticity of the free energy, which describes (initially only continuous) phase transformations [9, 10]. Within this framework, we postulate a Landau free energy *functional* which depends on the order parameters $\vec{\eta}$, encoding the extent of the transformation, and the coupling constants between them. We refer the keen reader to Ref. 10 for an excellent introduction.

Mean Field Theory

In this section, we apply the phenomenological Landau theory to a spatially homogeneous system to recover a mean field solution for the most likely order parameter by minimizing the Landau functional, and in doing so review the relevant literature.

The symmetry of the produce phase yields crystallographically equivalent martensitic variants, the number of which is given by the ratio of the proper rotations between the two phases, $n = P_A/P_M$ [6]. We therefore define an n-component order parameter to parametrize this coset space and expand our Landau functional in, $\vec{m}(x) = \{m_1(x), m_2(x), ..., m_n(x)\}$ [1]. Intuitively, each of the components describes a long range order parameters which has a non-zero value within a specific martensitic variant phase and vanishes within a different variant or austenite phase. For improper martensitic transformations the free energy is invariant under parity of the order parameters [1], $m_i \rightarrow -m_i$, and as such we define the order parameters to lie within $m_i \in [-1, 1]$ for convenience. It follows that the zero vector, $\vec{m} = \vec{0}$, describes the austenite phase.

We proceed by writing the three contributions to the Landau functional explicitly, namely the *elastic, chemical (thermal), and stress-induced* free energies:

$$F_{total} = F_{el} + F_{ch} + F_{st}. \tag{1}$$

In the limit of small displacements, the spontaneous lattice deformation can be described by crystallographic arguments alone by the Bain strain:

$$\epsilon_t(r) = \sum_{p=i}^{n} \theta_p(r)\epsilon_{ij}(p) = \sum_{p=i}^{n} m_p^2(r)\epsilon_{ij}(p), \tag{2}$$

where $\epsilon_{ij}(p)$ is the transformation tensor for the p^{th}

martensitic variant, and $\theta_p(r)$ is an arbitrary shape function. While $\theta_p(r)$ can in theory be expanded in all symmetry-preserving polynomial expansions [6–8], we limit ourselves to the lowest quadratic term. The elastic free energy contribution is then given by:

$$F_{el} = \frac{V}{2}\epsilon_t(r) : C : \epsilon_t(r) \tag{3}$$

$$= \frac{V}{2}\sum_{p=1}^{n} C_{ijkl}\epsilon_{ij}(p)\epsilon_{kl}(p)m_p^2(r)\varphi_p, \tag{4}$$

where C is the stiffness tensor, V is the total volume, φ_p is the volume fraction of the p^{th} variant, and the ($n = 24/8 =$)3 transformation tensors for the cubic-tetragonal transition are given by (and permutations thereof):

$$\epsilon_{t1} = \begin{pmatrix} \varepsilon_3 & 0 & 0 \\ 0 & \varepsilon_1 & 0 \\ 0 & 0 & \varepsilon_1 \end{pmatrix} \tag{5}$$

where

$$\varepsilon_1 = \frac{a_t - a_c}{a_c} \qquad \varepsilon_3 = \frac{c_t - a_c}{a_c} \tag{6}$$

a_t, c_t are the tetragonal crystal parameters, a_c is the cubic crystal parameter.

Similarly, the stress-induced contribution to the free energy is simply:

$$F_{st} = -\frac{1}{2}\sigma : \lambda : \sigma, \tag{7}$$

where $\sigma : \lambda = \sigma_{ij}\lambda_{jikl}$ is the two indices contraction of the stress and compliance tensors.

While the stress and elastic free energies only depends on the relative volume fractions of the variants, the chemical free energy is spatially inhomogeneous:

$$F_{ch} = \int d^d x \frac{1}{2}\sum_{p=1}^{n} k_{\alpha\beta}(p)\nabla_\alpha m_p \nabla_\beta m_p + f[\vec{m}(x)] \tag{8}$$

where $k_{ij}(p)$ are the positive definite gradient terms controlling fluctuations, ∇_α is the differential operator along the cartesian direction α, and $f[\vec{m}(x)]$ is a polynomial expanded in orders of the order parameters, preserving the symmetry of the austenite phase. In particular, we require that $f[\vec{m}(x)]$ have a local (metastable) minimum at the austenite phase ($\vec{m} = \vec{0}$), and 2n degenerate global minima at each martensite variant ($m_i = \pm\bar{m}, m_{j\neq i} = 0$). The simplest *2-4-6* polynomial which satisfies these requirements for the $n = 3$ cubic-tetragonal transition is [1]:

$$f(m_1, m_2, m_3) = \frac{t}{2}\vec{m}^2(x) + u\sum_{p=1}^{n=3} m_p^4(x) + v\left(\vec{m}^2(x)\right)^3 \tag{9}$$

where t, u, v are phenomenological parameters. We note that the quartic term breaks rotational symmetry and leads to the correct 2n-fold degeneracy ($\vec{m} = \pm\bar{m}\hat{e}_i$) for negative values of u.

In principle, one can now minimize the total free energy in the saddle point approximation and obtain mean-field criteria for the $A \Leftrightarrow M_i$ and $M_i \Leftrightarrow M_j$ transitions [6–8, 11–15]. Instead, we note that F_{stress} and F_{el} are positive contributions, and focus on the chemical contribution alone, from which it's easy to show that we obtain a first order transition for [10]:

$$u < 0, \qquad t^* = \frac{u^2}{2v} \tag{10}$$

with an order parameter discontinuity of

$$\Delta\bar{m} = \left(\frac{-u}{2v}\right)^{1/2} \tag{11}$$

While the above mean field theory correctly predicts the criteria for the transitions, we wish to investigate whether fluctuations around this saddle point destroy the ordered martensite phases, lead to collective Goldstone modes, and promote transitions between martensite variants. In order to do so, we will use statistical field theory methods like the Gaussian theory, momentum-space renormalization group and perturbation theory [9, 10]. These methods are usually employed in describing critical exponents which arise from continuous phase transitions. To justify our use of such methods, we note that the *2-4-6* potential in eq. (8) describes a tricritical point (separating first order and continuous phase transitions) in the limit as $u \to 0$ [10]. We require a non-zero value to u to enforce the underlying symmetry of our system, so the results henceforth should be considered in the limit of approaching the tricritical point from below.

Importance of Fluctuations

We introduce fluctuations around one of the ordered martensite variants M_i, along both the longitudinal directions (variations of m_i) and along the $n-1$ transverse directions (variations of $m_{j\neq i}$):

$$\vec{m}(x) = \left(\bar{m} + \phi_l(x)\right)\hat{e}_l + \sum_{\alpha=2}^{n}\phi_t^\alpha(x)\hat{e}_\alpha \tag{12}$$

and expand the terms in eq. (8), assuming $k_{ij}(p) = k\delta_{ij}$

$$(\nabla\vec{m})^2 = (\nabla\phi_l)^2 + \sum_{\alpha=2}^{n}\left(\nabla\phi_t^\alpha\right)^2 \tag{13}$$

$$(\vec{m})^2 = \bar{m}^2 + \cancel{2\bar{m}\phi_l} + \phi_l^2 + \sum_{\alpha=2}^{n}\left(\phi_t^\alpha\right)^2 \tag{14}$$

$$\sum_{p=1}^{n} m_p^4 = \bar{m}^4 + \cancel{4\bar{m}^3\phi_l} + 6\bar{m}^2\phi_l^2 + \cancel{4\bar{m}\phi_l^3} + O(\phi^4) \tag{15}$$

$$\left(\nabla\vec{m}^2\right)^3 = \bar{m}^6 + 15\bar{m}^4\phi_l^2 + 3\bar{m}^4\sum_{p=1}^{n}\left(\phi_t^\alpha\right)^2 + O(\phi^3), \tag{16}$$

where we've only kept the fluctuations contributing to second order. This allows us to split the free energy:

$$F_{ch}(\phi_l,\phi_t^\alpha) = F_{ch}(0,0) + \int d^dx\left\{\frac{k}{2}(\nabla\phi_l)^2 + \frac{\phi_l^2}{2}\left(t + 12\bar{m}^2u + 30\bar{m}^4v\right) + \sum_{\alpha=2}^{n}\left[\frac{k}{2}\left(\nabla\phi_t^\alpha\right)^2 + \frac{\left(\phi_t^\alpha\right)^2}{2}\left(t + 6v\bar{m}^4\right)\right]\right\} \tag{17}$$

$$= F_{ch}(0,0) + \begin{cases}\frac{n}{2}\int\frac{d^dq}{(2\pi)^d}ln(kq^2+t) & t>0\\ \frac{n}{2}\int\frac{d^dq}{(2\pi)^d}ln(kq^2-4t) & t<0\end{cases}, \tag{18}$$

where we've switched to a (Gaussian) Fourier-space representation on the second line, and identified longitudinal and transverse inverse correlation lengths as equivalent:

$$\xi_l^{-2} = \xi_{t,\alpha}^{-2} = \begin{cases}\frac{t}{k} & t>0\\ \frac{-4t}{k} & t<0\end{cases} \tag{19}$$

The no-zero transverse correlation lengths suggest that there are indeed restoring forces and collective Goldstone modes do not develop in the ordered martensite variants. This is a natural consequence of our quartic tem in eq. (9), which causes the broken symmetry to be discrete rather than continuous [10]. Differentiating eq. (18) wrt t, allows us to identify the diverging fluctuation corrections to the heat capacity as:

$$C_{fl} = C - C_{sp} \propto k^{-d/2}\,|t|^{d/2-2} \tag{20}$$

$$C_{sp} \propto (-tv)^{-1/2}u^3, \tag{21}$$

which identifies the Ginzburg criterion as in eq. (22), and the upper critical dimension as $d_u = 3$:

$$(-t)^{d-3} \gg \frac{k^d u^6}{v} \tag{22}$$

$$F_{ch} = \int\frac{d^dq}{(2\pi)^d}\frac{t+kq^2}{2}m(q)m(-q) + u\int\frac{d^dq_1d^dq_2d^dq_3}{(2\pi)^{3d}}m_i(q_1)m_i(q_2)m_i(q_3)m_i(-q_1-q_2-q_3) \tag{23}$$

$$+ v\int\frac{d^dq_1d^dq_2d^dq_3d^dq_4d^dq_5}{(2\pi)^{5d}}m_i(q_1)m_i(q_2)m_j(q_3)m_j(q_4)m_k(q_5)m_k(-q_1-q_2-q_3-q_4-q_5) \tag{24}$$

ϵ-expansion

In the previous section we've seen that for $d = 3$, where most of the martensitic transformations occur, the martensitic order obtained using a mean-field approach may be destroyed by fluctuations. In this section, we treat eq. (17) perturbatively and find recursion relations using an ϵ-expansion for $\epsilon = 4 - d$. The full free energy in Fourier space is given by eq. (24), where we identify the second and third terms as perturbations $\mathcal{U}$ and $\mathcal{V}$ respectively. We coarse grain by a factor of b, subdiving our momenta into two components $\left\{\tilde{\vec{m}}\right\} = \{\vec{m}\}\oplus\{\vec{\sigma}\}$ and expand the products in eq. (24) to obtain the first and second cumulants of $\mathcal{U}$ and $\mathcal{V}$. We represent the summation diagrammatically, using the four- and six-leg vertices shown in Fig. 1 (see also Fig. 2). Most of the diagrams don't contribute to the renormalization procedure either due to their parity, momentum conservation, or the order of their inner loop integrations. Omitting diagrams of order q^2m^4, q^2m^6, etc., the contributions are shown schematically in Fig. 1. Contribution *(vi)* for example is calculated as:

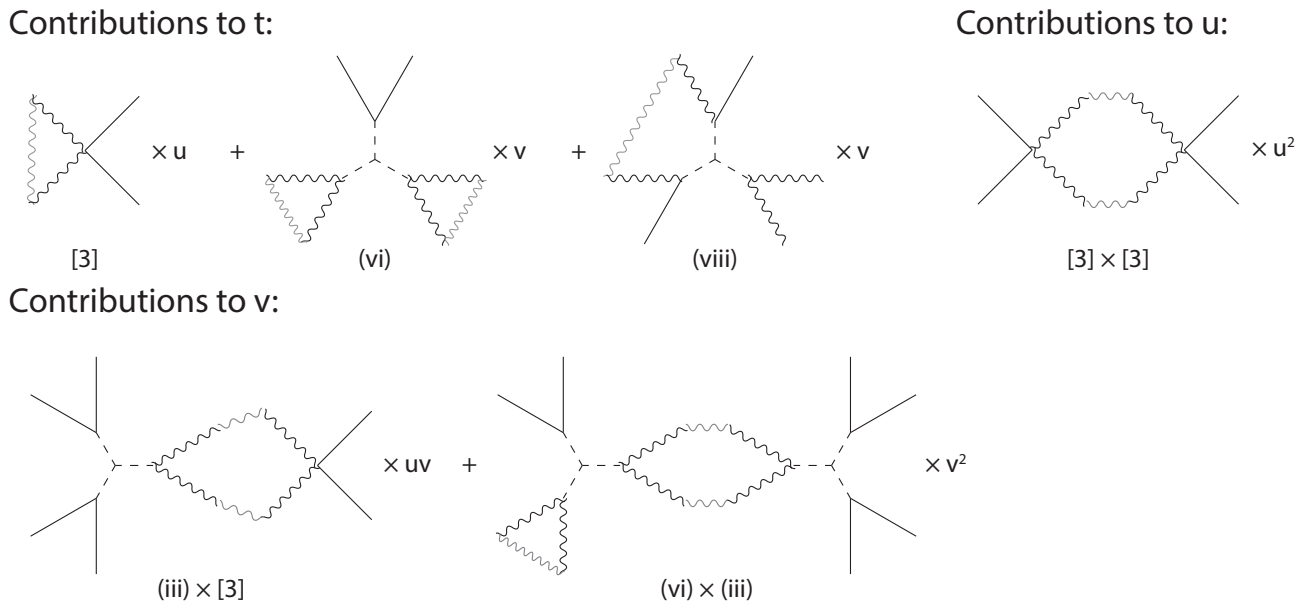

Fig. 1. **Contributing diagrams to second order in $\mathcal{U},\mathcal{V}$.** Short wavelength fluctuations are wavy, with contractions shown in gray.

$$-2v\int \frac{d^dq_1\dots d^dq_6}{(2\pi)^{6d}}(2\pi)^d\,\delta^d(q_1+\dots+q_6)\frac{\delta_{jj}\,(2\pi)^d\,\delta^d(q_5+q_6)}{t+kq_5^2}\frac{\delta_{ii}\,(2\pi)^d\,\delta^d(q_3+q_4)}{t+kq_3^2}m(q_1)\cdot m(q_2) \tag{25}$$

$$=-2n^2v\int_0^{\Lambda/b}\frac{d^dq}{(2\pi)^d}\,|m(q)|^2\int_{\Lambda/b}^{\Lambda}\frac{d^d\kappa}{(2\pi)^d}\frac{1}{\left(t+k\kappa^2\right)^2} \tag{26}$$

Similar calculations for each of the six contributing diagrams lead to three coarse-grained parameters. After the usual rescaling and renormalizing steps of RG [9], we obtain the following recursion relations:

$$\begin{cases}\frac{dt}{dl}=2t+\frac{4unK_d\Lambda^d}{t+k\Lambda^2}-\frac{\left(2n^2+4n\right)vK_d\Lambda^d}{\left(t+k\Lambda^2\right)^2}\\ \frac{du}{dl}=(4-d)u-\frac{36u^2vK_d\Lambda^d}{\left(t+k\Lambda^2\right)^2}\\ \frac{dv}{dl}=(6-2d)v-\frac{48nuvK_d\Lambda^d}{\left(t+k\Lambda^2\right)^2}-\frac{32n^2v^2vK_d\Lambda^d}{\left(t+k\Lambda^2\right)^3}\end{cases} \tag{27}$$

Setting eq. (27) to zero yields four fixed points, including the Gaussian one ($t^*=u^*=v^*=0$), a fixed point with destroys the ordered phase ($u^*=0$), a fixed point which removes the sectic term ($v^*=0$), and one where all parameters are non-zero. Linearizing the recursion relations around each fixed point reveals that the only stable one, for $n=3$ and $\epsilon=4-3=1$, is the one with $v^*=0$ with eigenvalues $\lambda_t=2-\frac{n\epsilon}{9},\lambda_u=-\epsilon,\lambda_v=\epsilon\left(2-\frac{4n}{3}\right)-2$. This suggests that fluctuations about the saddle point solution do not destroy the ordered martensite phase, at this order of perturbation.

Concluding Remarks

Much of the existing literature on martensitic transformations deals with the spatially-homogeneous system, arriving at mean-field solutions. It is a sobering thought that as we approach the tricritical point, the upper critical dimension such solutions would be valid in is $d=3$. In this paper, we investigated martensitic transformations beyond mean field by including longitudinal and transverse fluctuations. Reassuringly, we find the existence of a stable fixed point upon renormalization with a non-zero quartic term, suggesting that indeed martensitic variants obtained using mean-field solutions are stable at $d=3$.

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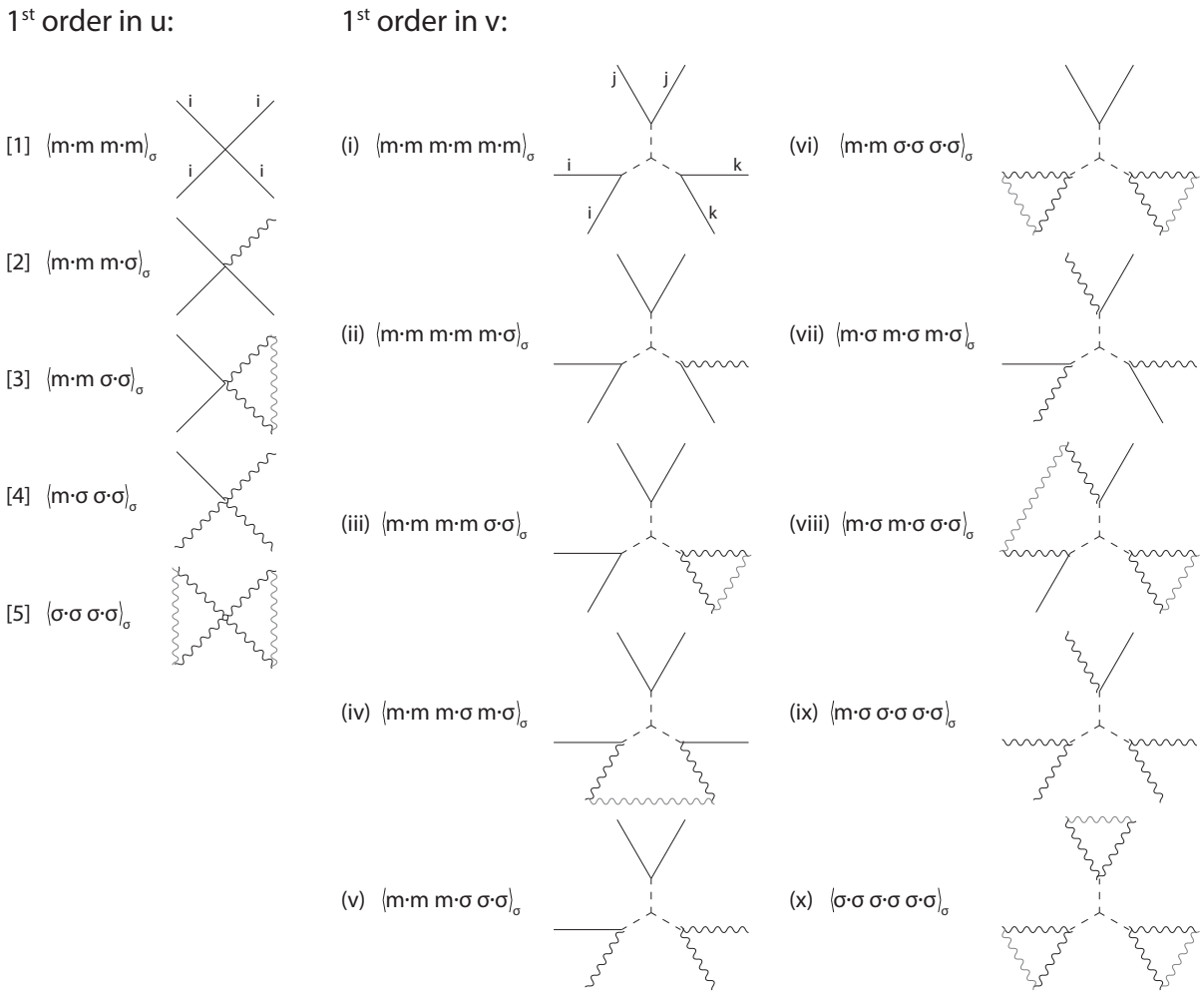

Fig. 2. First order contractions in $\mathcal{U}$ and $\mathcal{V}$.

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