Monte Carlo simulations of vector pseudospins for strains: Microstructures and martensitic conversion times

N. Shankaraiah

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India.

Abstract

We present systematic temperature-quench Monte Carlo simulations on discrete-strain pseudospin model Hamiltonians to study microstructural evolutions in ferroelastic transitions with two-component vector order parameters ($N_{OP} = 2$) in 2-spatial dimensions. The zero value pseudospin is the single high-temperature phase while the low-temperature phase has $N_v$ variants. Thus the number of nonzero values of pseudospin are triangle-to-centered rectangle ($N_v = 3$), square-to-oblique ($N_v = 4$) and triangle-to-oblique ($N_v = 6$). The model Hamiltonians contain a transition-specific Landau energy term, a domain wall cost or Ginzburg term, and power-law anisotropic interaction potential, induced from a strain compatibility condition. On quenching below a transition temperature, we find behaviour similar to the previously studied square-to-rectangle transition ($N_{OP} = 1, N_v = 2$), showing that the rich behaviour found, is generic. Thus we find for two-component order parameters that the same Hamiltonian can describe both athermal and isothermal martensite regimes for different material parameters. The athermal/isothermal/austenite parameter regimes and temperature-time-transformation diagrams are understood, as previously, through parametrization of effective-droplet energies. In the athermal regime, we find rapid conversions below a spinodal-like temperature and austenite-martensite conversion delays above it, as in the experiment. The delays show early incubation behaviour, and at the transition to austenite the delay times have Vogel-Fulcher divergences and are insensitive to Hamiltonian energy scales, suggesting that entropy barriers are dominant. Systematic temperature quench experiments can look for martensite formation and growth during conversion-incubations, divergences, and distributions close to the transition.

Keywords: martensites, athermal, isothermal, Monte Carlo, strain, TTT curves

MSC codes here, in the form:

2000 MSC: code, code or
2008 MSC: code, code (2000 is the default)

1. Introduction

Steels, shape memory alloys and high-$T_c$ superconductors are martensitic materials that undergo diffusionless, first-order phase transformation from high-temperature parent 'austenite' unit-cell to low-temperature product 'martensite' unit-cells (or variants) on cooling or under external stress [1]. A subset of physical strains are the order parameter (OP). As martensitic materials have many applications [1, 2], much work has been done to understand domain-wall microstructures and their underlying kinetics. According to traditional classification [3], martensites are classified as athermal, with rapid milli-second austenite-martensite conversions on cooling below a martensite start temperature and no conversions above it; and isothermal, which can have slow or delayed conversions in minutes or hours. But, experiments on athermal martensitic materials have found delayed conversions above the martensite start temperature, where only austenite should exist [4]. Computer simulations of martensitic models could give insights into the classification and the unexpected delays in athermal martensites.

Continuous variable nonlinear free energies are minimized in displacement, phase field, and strain using relaxational dynamics, Monte Carlo (MC) and Molecular dynamics simulations [5, 6, 7, 8, 9] and the obtained microstructures are consistent with experiments [10], but that can need extensive computer time. More economic discrete-strain clock-like model Hamiltonians [11] are systematically derived from continuous-strain free energies for different ferroelastic transitions in 2- and 3-spatial dimensions (2D & 3D). Power-law anisotropic interaction potentials, which arise from the no-defect St.Venant compatibility condition [11, 12], and orient strain domain walls, have their counterparts induced in pseudo spin Hamiltonians. The microstructures generated from these strain-pseudospin models using local mean-field [13] are in good agreement with continuous variable models [5, 6, 7] and experiments [10].

Systematic temperature-quench MC simulations were performed on the simplest single-component or scalar-OP, 3-state pseudospin Hamiltonian for square-to-rectangle (SR) transition [14] and showed both rapid conversions below a spinodal-like temperature and incubation-delays above it, as in experiments [4] on athermal martensitic materials. The conversion-time delays are found to have Vogel-Fulcher divergences, which are
insensitive to Hamiltonian energy scales and log-normal distributions, suggesting the dominant role of entropy barriers. An athermal/isothermal martensites regime diagram is predicted in material parameters; crossover temperatures and domain-wall phases in Temperature-Time-Transformation (TTT) diagrams are understood through parametrization of textures by surrogate droplet energies; and role of power-law potentials is shown to be important for textures and incubations [14]. The central question is: Are such conversion-delays in athermal martensite regime, specific to the scalar-OP transition, or are they generic, appearing in two-component vector-OP transitions?

In this paper, we show that the athermal martensite regime conversion-delays in the scalar-OP \( (N_{OP} = 1) \) SR transition are generic in three vector-OP \( (N_{OP} = 2) \) ferroelastic transitions: triangle-centered rectangle \( (N_t = 3) \); square-oblique \( (N_t = 4) \); triangle-oblique \( (N_t = 6) \). Under systematic MC temperature quenches, we find isothermal parameter regime with slow or delayed conversions and athermal parameter regime that has rapid conversions below a temperature and incubation-delays above it, as in experiments [4] and the scalar-OP SR transition [14]. The athermal regime conversion-time delays have Vogel-Fulcher divergences, which are insensitive to Hamiltonian energy scales. The athermal/isothermal/austenite regime diagrams are obtained in material parameters. The crossover temperatures and domain-wall phases in the TTT diagram are understood through the parametrization of textures. Microstructures obtained in these transitions are in good agreement with continuous-variable simulations [5, 6, 7] and experiments [10]. We finally show the importance of power-law interaction potentials in the incubation behaviour, and microstructures.

The paper is organised as follows. In Section 2, we outline derivations of the vector-OP strain-pseudospin Hamiltonians. In Section 3, we present the athermal/isothermal martensite regimes and crossover in material parameters. In Section 4, we focus on the athermal martensite regime and present conversion-delay kinetics, parametrization of domain-wall phases in TTT diagram by effective droplet energies, and conversion incubation textures. In Section 5, we present kinetics in the absence of the power-law anisotropic interactions that shows delays without incubation, and Section 6 is a summary.

2. Strain-pseudospin Hamiltonians

In this Section, we state the vector-OP strain-pseudospin model Hamiltonians [11] that were systematically derived from scaled continuous-strain free-energies [12] for triangle-centered rectangle (TCR), square-to-oblique (SO) and triangle-to-oblique (TO) ferroelastic structural transitions.

The distortions of a 2D unit cell can be described by \( d(d + 1)/2 = 3 \) or three distinct physical strains, compressional \( (e_1) \), deviatoric \( (e_2) \) and shear \( (e_3) \) that are linear combinations of Cartesian strain tensor components \( e = [e_{\mu\nu}] \),

\[
e_1 = (e_{xx} + e_{yy})/\sqrt{2}, \quad (2.1a)
\]

\[
e_2 = (e_{xx} - e_{yy})/\sqrt{2}, \quad (2.1b)
\]

\[
e_3 = e_{xy}, \quad (2.1c)
\]

where \( e_{xx}, e_{yy} \) are stretches and \( e_{xx}, e_{yy} \) are tilts of a unit cell along \( x \) and \( y \) directions. Of these, \( (e_2, e_3) \) are OP \( (N_{OP} = 2) \) and the \( e_1 \) is non-OP \( (n = 1) \) strains.

The scaled free energy has a Landau term \( \tilde{F}_L \); a Ginzburg term, quadratic in the OP gradients \( \tilde{F}_G \); and a seemingly innocuous term, quadratic in the non-OP strains \( \tilde{F}_{non} \) that turns out to generate crucial power-law anisotropic interactions between the OP strains [11]. Thus

\[
F = E_0[\tilde{F}_L + \tilde{F}_G + \tilde{F}_{non}], \quad (2.2)
\]

where \( E_0 \) is an elastic energy per unit cell. The transition specific Landau term \( \tilde{F}_L \) has \( (N_t + 1) \) degenerate energy minima at the first-order transition as shown in Figure 1. The high-temperature austenite minimum is allowed at all temperatures as its existence has to be determined dynamically, and \( N_t \) minimum are the low-temperature martensite variants.

![Figure 1: Landau free energy minima and strain-pseudospin clock vectors: (a) Contours of Landau free energy \( \tilde{F}_L \) showing single austenite minimum at center and \( N_t \) martensite minima at corners, in a plot of \( e_3 \) versus \( e_2 \) and (b) corresponding clock model minima at pseudospin values for TCR (left), SO (middle) and TO (right) transitions.](image)

The scaled Landau free energy \( \tilde{F}_L \) for TCR transition [11]

\[
\tilde{F}_L(\vec{e}) = \sum_{\ell} \left((\tau - 1)\tilde{e}^2 + [\tilde{e}_2^2 - 2(\tilde{e}_2^2 - 3\tilde{e}_2\tilde{e}_3) + (\tilde{e}_3^2)]\right), \quad (2.3)
\]

has an austenite minimum at \( (e_2, e_3) = (0, 0) \), and \( N_t = 3 \) martensite minima at which \( (e_2, e_3) = (\cos \phi, \sin \phi) \) for \( \phi = 0, \frac{2\pi}{3}, \frac{4\pi}{3} \). Here \( \tilde{e}_2 = e_2 + e_3 \) and \( \tau = (T - T_c)/(T_0 - T_c) \) is the scaled temperature; \( T_0 \) is the first-order Landau transition temperature and \( T_c \) is metastable austenite spinodal temperature.

The scaled Landau free energy \( \tilde{F}_L \) for SO transition [11]

\[
\tilde{F}_L(\vec{e}) = \sum_{\ell} \left((\tau - 4 - C_s/2)\tilde{e}^2 + 4\tilde{e}^2 - C_4\tilde{e}_2^2\tilde{e}_3^2\right), \quad (2.4)
\]

also has an austenite minimum at \( (e_2, e_3) = (0, 0) \), and \( N_t = 4 \) martensite minima at which \( (e_2, e_3) = (\cos \phi, \sin \phi) \) for \( \phi = \frac{\pi}{4}, \frac{3\pi}{4}, \frac{5\pi}{4}, \frac{7\pi}{4} \) with material dependent elastic constant \( C_s \).
The scaled Landau free energy for TO transition [11] is
\[ F_L(\vec{\varepsilon}) = \sum_{\ell} (\tau - 1)\vec{\varepsilon}_\ell^2 + \tilde{\alpha}(\vec{\varepsilon}_\ell^2 - 1)^2 + C_6(\vec{\varepsilon}_\ell^2 - (e_1^2 - 3e_2e_3^2)\), \] (2.5)
where \( C_6 \) is a material dependent parameter. The Landau polynomial has an austenite minimum at \((e_2, e_3) = (0, 0)\), and \( N_c = 6 \) martensite minima at which \((e_2, e_3) = (\cos \phi, \sin \phi)\) for \( \phi = 0, \frac{\pi}{6}, \frac{\pi}{3}, \frac{\pi}{2} \) and \( \frac{2\pi}{3} \).

The domain-wall cost Ginzburg term \( \tilde{F}_{GW} \) is,
\[ \tilde{F}_{GW}(\vec{\nabla}\vec{\varepsilon}) = \xi^2 \sum_{\vec{r}} (\vec{\nabla}\vec{\varepsilon})^2, \] (2.6)
where \( \xi \) is the domain wall thickness.

The non-OP term is harmonic [11], with stiffness \( A_1 \),
\[ \tilde{F}_{non}(e_1) = \sum_{\vec{r}} A_1 \frac{\nu}{2} e_1^2 - \sum_{\vec{r}} A_1 \frac{\nu}{2} |e_1|^2 \] (2.7)
and is minimized subject to St.-Venant compatibility constraint for physical strains [12] that says no dislocations are generated during distortion of the unit cells throughout the system,
\[ \Delta^2 e_1 - (\Delta^2 e_1 - \Delta^2 e_2 - 2\Delta e_3) = 0; \] (2.8a)
with gradient terms as difference operators \( \vec{\nabla} \rightarrow \vec{\Delta} \) for sites \( \vec{r} \) on a computational grid. In Fourier space \( k_{\mu} \rightarrow K_{\mu}(\vec{k}) \equiv 2\pi n(k_{\mu}/2) \) and so
\[ O_1 e_1 + O_2 e_2 + O_3 e_3 = 0, \] (2.8b)
where the coefficients are \( O_1 = -\frac{1}{\sqrt{2}} K^2, O_2 = \frac{1}{\sqrt{2}} (K^2 - K^2), \) and \( O_3 = 2K^2K_s \) for square lattice; and \( O_1 = -K^2, O_2 = (K^2 - K^2), \) and \( O_3 = 2K^2K_s \) for triangle lattice. Here, \( K^2 = (K^2 + K^2) \). The stiffness \( A_1 \) is related to the Voigt elastic constants, for example, \( A_1 \sim (C_{11} + 2C_{12})/(C_{11} - C_{12}) \), and is proportional to the elastic anisotropy parameter \( 2C_{44}(C_{11} - C_{12}) \).

Minimization of non-OP strains generates power-law interactions between the OP strain that orient the domain walls in preferred crystallographic directions, by inserting a direct solution \( e_1 = -(O_2 e_2 + O_3 e_3)/O_1 \) for \( \vec{k} \neq 0 \) into (2.6),
\[ F_{\text{compad}}(e_2, e_3) = A_2 \sum_{\ell,\ell^\prime} e_1(\vec{k}) U_{\ell\ell^\prime}(\vec{k}) e_{\ell^\prime}(\vec{k}) \] (2.9)
where \( U_{\ell\ell^\prime}(\vec{k}) = v(O_2/O_1)^2, U_{22}(\vec{k}) = v(O_2/O_1)^2, U_{23}(\vec{k}) = v(O_2/O_1)^2 \) and \( v = 1 - \delta e_0 \). Figure 2 shows the power-law anisotropic potentials \( U_{\ell\ell^\prime} \) as relief plots in Fourier space and contours in coordinate space.

The continuous-strain OP \( \vec{\varepsilon} = (e_2, e_3) \) is discretized [11] by choosing its values only at the \( N_c + 1 \) Landau minima,
\[ \vec{\varepsilon}(\vec{r}) = |e| (\cos \phi, \sin \phi) \rightarrow \vec{\varepsilon}(\tau)\vec{S}(\vec{r}). \] (2.10)

The Landau term [11] becomes,
\[ H_L(\vec{S}) = \tilde{\varepsilon}^2 \sum_{\tau} g_{L}(\tau)\vec{S}^2(\vec{r}) = \tilde{\varepsilon}^2 \sum_{\tau} g_{L}(\tau)|\vec{S}(\vec{r})|^2 \] (2.11)
where \( g_{L} = \tau - 1 + (\tilde{\varepsilon}^2 - 1)^2 = \frac{1}{2}[1 + \sqrt{1 - 8\tau/9}] \) for TCR, and \( g_{L} = \tau - 1 + (\tilde{\varepsilon}^2 - 1)^2 = \frac{1}{2}[1 + \sqrt{1 - 3\tau/4}] \) for SO and TO transitions.

The square gradient Ginzburg term becomes,
\[ H_{GW}(\vec{S}) = \xi^2 \sum_{\tau} \vec{\varepsilon}^2(\vec{S}^2(\vec{r})) = \xi^2 \sum_{\tau} K^2 \tilde{\varepsilon}^2|\vec{S}(\vec{r})|^2 \] (2.12)

The discrete-strain pseudospin model Hamiltonian is derived [11] by substituting (2.9) into the total free energy (2.1),
\[ \beta H(\vec{S}) \equiv \beta F(\vec{\varepsilon} \rightarrow \vec{S}) \] (2.13)

The Hamiltonian in coordinate space is
\[ \beta H = \frac{D_0}{2} \sum_{\tau} \{ g_{\ell\ell^\prime}(\tau)\vec{S}^2(\vec{r}) + \xi^2(|\vec{S}|^2)^2 \} \]
\[ + \sum_{\ell,\ell^\prime} \frac{A_1}{2} U_{\ell\ell^\prime}(\vec{r}) \vec{S}_{\ell}(\vec{r})\vec{S}_{\ell^\prime}(\vec{r}), \] (2.14a)
where \( D_0 = 2E_0\tilde{\varepsilon}^2 \). It is diagonal in Fourier space,
\[ \beta H = \frac{1}{2} \sum_{\ell,\ell^\prime} \sum_{\vec{k}} Q_{0,\ell\ell^\prime}(\vec{k})\vec{S}_{\ell}(\vec{k})\vec{S}_{\ell^\prime}(\vec{k}) \] (2.14b)
\[ Q_{0,\ell\ell^\prime}(\vec{k}) \equiv D_0[|g_{\ell\ell^\prime}(\tau) + \xi^2\vec{R}^2|\delta_{\ell,\ell^\prime} + \frac{A_1}{2} U_{\ell\ell^\prime}(\vec{k})], \] (2.14c)
and is a clock-zero model Hamiltonian with single austenite \( \vec{S} = (S_2, S_3) = (0, 0) \) and \( N_c \) martensite variants:
\[ \vec{S} = (1, 0), (-1, \frac{\sqrt{3}}{2}; \pm \frac{\sqrt{3}}{2}; \pm \frac{\sqrt{3}}{2}; \pm \frac{\sqrt{3}}{2}; \pm \frac{\sqrt{3}}{2}; \pm \frac{\sqrt{3}}{2}); \pm \frac{\sqrt{3}}{2} \) \] (2.15)
for TCR, \( N_c + 1 = 4 \), SO \( N_c + 1 = 5 \), and TO \( N_c + 1 = 7 \) transitions respectively.

MC temperature-quench simulations are carried out systematically [14] on a square lattice in 2D. At \( t = 0 \), we consider 2% of sites randomly with \( N_c \) strain-pseudospin martensite values.
in austenite. The seeds are quenched below the Landau transition \( \tau \ll 1 \) and held for \( t \leq t_h \) MC sweeps (MCS). Metropolis algorithm is used for acceptance of energy changes that are calculated through Fast Fourier transforms. In each MC sweep, we visit all \( N = L \times L \) sites randomly, but only once. Simulation parameters are \( L = 64, T_0 = 1; T_c/T_0 = 0.6, 0.7, 0.8, 0.9, \xi = 1; A_1 = 1, 4, 10; 2A_1/A_3 = 1; E_0 = 3, 4, 5, 6; t_h \leq 10,000 \) MCS, and conversion times are averaged over \( N_{\text{runs}} = 100 \) runs.

3. Athermal and isothermal parameter regimes

On quenching 2% of martensite seeds to a temperature \( \tau(T) < \tau(T_0) \), we define [14] martensite conversion fraction \( n_m(t) \), which is equal to 0 in the pure austenite and 1 in the pure/twinned martensite,

\[
n_m(t) = \frac{1}{N} \sum_{\vec{r}} S^2(\vec{r}), \quad (3.1)
\]

and specify conversion time \( t = t_m \) when \( n_m(t_m) = 0.5 \).

Figure 3 shows isothermal slow conversions and athermal fast conversions with incubation-delay tails for different material parameters \( A_1, T_c/T_0 \) in TCR, SO, and TO transitions. Figure 3 also shows crossover from athermal to isothermal by fixing \( A_1 \) and changing \( T_c/T_0 \), and vice versa. Hence, we find the martensite classification is a matter of material parameters as in the SR case[14]: the same model Hamiltonian can show both athermal or isothermal behaviour, dependent on parameters.

The athermal/isothermal/austenite regime diagrams are obtained in material parameters \( T_c/T_0, A_1 \) and shown in Figure 4 that clearly depicts athermal martensites are more common than isothermal [2]. The simulations data matches well with the estimates [14] of theoretical boundaries. Here, the criterion for athermal is \( \bar{t}_m = 10 \) MCS; isothermal/intermediate is \( \bar{t}_m = 1000 \) MCS; and austenite, if there are no conversions even for holding time \( t = t_h \). Again this is just as in the SR case [14].

We will focus on the athermal regime. Figure 5 shows single-seed runs of \( n_m(t) \) vs \( t \) after quenches to various \( \Delta \tau \equiv \tau - \tau_4 < 0 \), below the transition temperature \( \tau_4 \equiv \tau(T_4) \). At low temperatures, \( n_m(t) \) rises rapidly to unity, but as transition is approached, shows incubation behaviour. In the case of TCR tran-
sition, $m(t)$ rises to a smaller value that incubates for longer times before it rises sharply to unity. In SO transition, $m(t)$ shows incubation followed by jerky steps before it rises to unity. In TO transition, $m(t)$ has longer incubations before it sharply rises to unity. The transition is 'fuzzy' and is operationally defined as where all 100 runs give austenite. Hence, we define

\[ r_{\text{SO}} \equiv \frac{t_{\text{SO}}}{t_{\text{SO}}} < 1/100 \text{, where mean conversion rate} \]

\[ r_{\text{SO}} \equiv \frac{t_{\text{SO}}}{t_{\text{SO}}} > 1/100 \text{ is obtained by an arithmetic average over} \]

\[ N_{\text{runs}} = 100 \text{ seeds.} \]

We henceforth focus on the athermal martensite parameter regime to study the conversion incubation-delays kinetics.

### 4. Textural energies parametrized by surrogate droplets

The transition is known to depend both on temperature and the size of martensite seeds, as in the Pati-Cohen model [3]. In early work, Pati and Cohen [3] have measured and modeled the conversion times in Ni-Mn alloys and found that the isothermal slow conversions can change to athermal fast conversions, for fixed martensite fraction, but with larger (and hence fewer) initial martensite seeds. This can be understood through the parametrization of textural droplet energies as in the SR transition [14]. At $t = 0$, the seeds of $N_s$ variants are randomly sprinkled throughout the lattice. We find that the interaction tend to cancel leaving only self-interaction part $A_1[U]/2$ at each seed. So we have,

\[ H[S(0)] = -2 \sum_{\vec{r}} [g]_i S(0) \vec{r} + \frac{A_1[U]}{2} S(0) \vec{r}^2. \]

Here $[U] \equiv 0.5$, is the Brillouin-zone average of $U(\vec{k})$ of (2.8) in TCR, SO, and TO transitions. For an initial martensite fraction $m(0) = 0.02$, we have $N_s$ variants square seeds of sides $R(0)$. The initial pseudospin seed energy is parametrized as $\beta H(S(0)) = C_0[1, \alpha G, R(0)]^2 + \alpha G[R(0) + c(A_1[U]/2)R(0)]^2$ with $C_0 \equiv (m(0)/ND_0)/2$. For different sides $R(0) = 1, 2, 3$, we fit the coefficients $\alpha, G, c$ term-by-term, finding again $\alpha_1 = \alpha_2 = \alpha_3 = 1$, independent of seed size. Then the initial energy has a droplet-like form $\beta H(R(0)) = C_0[2\alpha^2 R, 1 - (1-R(0)/R_c)]^2$. Here we define a length $R_0(\tau)$ that is positive below a divergence temperature $\tau = \tau_2(A_1)$,

\[ R_0(\tau) \equiv \frac{-2\alpha^2}{g_2(\tau) + A_1[U]/2}. \]

As in the SR case, we define a scaled temperature variable $\eta(\tau)$ from the parametrization

\[ \eta(\tau) = -R(0)/R_0(\tau) = \frac{g_2(\tau) + A_1[U]/2}{2\alpha^2}. \]

that will be used later, for $R(0) = 1$.

At $t = 0$, the initial seeds have a geometric meaning, and hence the pseudospin Hamiltonian $H[S(0)]$ matches the droplet Hamiltonian $H[R(0)]$, but for general $t$, these two terms no longer match term-by-term. However, as in the SR case, we define $R(t)$ through $H[S(t)]/H[S(0)] = H[R(t)]/H[R(0)]$. The energy (ratio) for interacting vector pseudospins is parametrized, by the energy (ratio) of a surrogate system of independent droplets. The initially geometric $R(t)$ evolves to an interacting-texture energetic parameter $R(t)$ that can even go negative as the pseudospin energy goes negative. Thus

\[ \rho(t) \equiv \beta H[S(t)]/\beta H[S(0)] \]

\[ = [1 - (R(t)/R_c - 1)^2]/[1 - (R(0)/R_c - 1)^2]. \]

The $R(t)$ evolution is then once again

\[ R(t)/R_c = 1 + \alpha \sqrt{1 - \rho(t)/\rho_c}, \]

where $\rho_c \equiv [1 - (R(0)/R_c - 1)^2]^{-1}$, and we take $\alpha = \text{sign}(R(0)/R_c - 1)$.

Figure 6 shows the evolutions of effective droplet energy in a plot of $R(t)/R_c(t)$ versus time. There are both rapid rises to final positive values and flat-incubations as already seen in the martensite conversion fraction $m(t)$, which goes negative at later times. The flat-incubations are due to the inefficient searches for the rare channels to lower energies. The initial $R(0)/R_c$ values determine the $R(t)$ flows.

As a consistency test of parametrization, Fig. 7 shows $\rho(t)/\rho_c$ versus $R(t)/R_c$ indeed matches a parabola, for all $t$, and all $A_1$, and many starting values $R(0)/R_c(t)$ in TCR, SO, and TO transitions. Flow directions of $R(t)$ are indicated by arrows starting

![](image-url)
at $R(0)/R_c$ for Regions 1, 2, 3, 4, with asymptotic $R(t)$ giving negative final martensitic energies, or zero (going to austenite).

i) Region 1: For initial $R(0)/R_c(\tau) > 2$, there are explosive conversions to martensite, this determines a temperature $\tau = \tau_1$ or $1/R_c(\tau_1) = 2$ or in scaled variable $\eta(\tau) = -2$ with initial unit seeds $R(0) = 1$.

ii) Region 2: For initial droplets $2 > R(0)/R_c(\tau) > 1$, the flows are again fast, this determines a temperature $\tau = \tau_2$ where $1/R_c(\tau_2) = 1$ or $\eta(\tau) = -1$.

iii) Region 3: For $0.5 \lesssim R(0)/R_c(\tau)$ or $\eta(\tau) \gtrsim -0.5$, the initial droplets are flowing only to $R = 0$ austenite. But, for larger $A_1$, the droplets can still grow through searches up to $R(0)/R_c(\tau) \approx 0$ or $\eta(\tau) \approx 0$ that is well below the Landau transition temperature $T_0$.

iv) Region 4: For $0.5 \lesssim R(0)/R_c(\tau) \lesssim 1$, the initial droplets immediately convert to a single variant droplet that incubates for long times around $R(t) \approx 0$ with zero energy $H \approx 0$ (degenerate with austenite). This entropically critical droplet searches for conversion pathways, and grows through jerky steps and elastic photocopying [11]. The incubations occur for unit seeds up to a temperature $\tau = \tau_4$ or $1/R_c(\tau_4) = 0.5$ or $\eta(\tau) = -0.5$.

This explains that for larger initial martensite seeds sizes the conversions are faster [3]. These critical values of the scaled variable $\eta(T, A_1)$ are used in the scaled plot of Fig. 8.

5. Athermal regime conversions

On quenching the system to a bath temperature $T$, it faces free-energy barriers while finding the global minimum out of a large number of metastable local minima and hence the re-equilibration $t \sim e^{\Delta S/T} \sim e^{\Delta U/T} e^{\Delta S}$. Theoretical boundaries (shown as dotted lines) in $\tau_1, \tau_2, \tau_4$ are defined by $R_c(\tau_{1,2,4}) = R_{4,2,4}$ of Fig 7 and symbols are data from simulations. See text.

Figure 7: Parametrization and crossover temperatures: Scaled pseudospin energy $\rho(t)/\rho_c$ versus $R(t)/R_c(\tau)$, showing flows fall on a parabola as a test of parametrization. For $R(0) = 1$ seeds, characteristic initial values $R(0)/R_c$ are $R_1^{-1} = 2, R_2^{-1} = 1, R_4^{-1} = 0.5$ as marked. These correspond to temperatures $\tau_1, \tau_2, \tau_4$. For initial $R(0)/R_c \lesssim 0.5$, flows are to $R = 0$ austenite.

Figure 8: Textural crossover temperatures: Phase diagram $R_0/R_c$ vs $A_1$. Theoretical boundaries (shown as dotted lines) in $\tau_1, \tau_2, \tau_4$ are defined by $R_c(\tau_{1,2,4}) = R_{4,2,4}$ of Fig 7 and symbols are data from simulations. See text.

Figure 6: Trajectories: Scaled energy parameter $R(t)/R_c$ versus time $t$, showing flows are determined by initial $R(0)/R_c(\tau)$ values. Note flat incubations of lower curves, of initial $1 > R(0)/R_c(\tau) > 0.5$, corresponding to $\tau_2 < \tau < \tau_4$ for TCR (left), SO (middle) and TO (right) transitions.
the solid line is Vogel-Fulcher times 

\[ t \]

Experimental conversion-delay times: Figure 9: Singular divergence of conversion times: (a) TCR, (b) SO and (c) TO transitions with \( T_0/T_0 = 0.9, E_0 = 3, 4, 5, 6 \) and \( A_1 = 1, 4, 10 \). Solid line is \( \ln t_m = \ln t_0 + b_0 (\tau - \tau_d)/|\Delta \tau| \), with \( t_0 = 1.6 \) and \( b_0 = 1.7 \). Inset: Plot of \( 1/\ln t_m \) vs \( |\Delta \tau|/|\tau_1 - \tau_d| \) showing linearity as \( |\Delta \tau| \to 0 \).

to diverge at a temperature \( \tau \approx \tau_d \). The conversion times for different values of material parameters \( A_1, E_0 \) fall on a single hyperbola in \( \ln t_m \) versus \( \Delta \tau \equiv \tau - \tau_d \), for a range of temperatures \( \tau_d < \tau < \tau_1 \) as shown in main Fig 9. The same data is plotted in inset as \( 1/\ln t_m \) versus \( |\Delta \tau|/|\tau_1 - \tau_d| \) that shows linearity on \( |\Delta \tau| \) goes to zero. The hyperbola and the linearity are showing the Vogel-Fulcher behaviour [15]. Specifically, \( t_m = t_0 \exp[b_0 (|\tau_1 - \tau_d|/|\tau - \tau_d|)] \), with \( t_0 = 1.6, b_0 = 1.7 \), for these data. The insensitivity of conversion times \( t_m \) to energy scales \( E_0 \) implies that the Vogel-Fulcher behaviour at \( \tau_d \) comes from divergence of entropy (rather than energy) barriers, \( t_m \sim \exp[|\Delta S_{\text{entr}}|] \) in finding the rare channels [16]. The entropy barriers then vanish at \( \tau_1 \), with a drop in conversion times.

Figure 9: Singular divergence of conversion times: Plot of \( \log t_m \) vs \( \Delta \tau = \tau - \tau_d \), for (a) TCR, (b) SO and (c) TO transitions with \( T_0/T_0 = 0.9, E_0 = 3, 4, 5, 6 \) and \( A_1 = 1, 4, 10 \). Solid line is \( \ln t_m = \ln t_0 + b_0 (|\tau_1 - \tau_d|)/|\Delta \tau| \), with \( t_0 = 1.6 \) and \( b_0 = 1.7 \). Inset: Plot of \( 1/\ln t_m \) vs \( |\Delta \tau|/|\tau_1 - \tau_d| \) showing linearity as \( |\Delta \tau| \to 0 \).

The measured conversion-delay times \( t \) (in hours) versus deviation from transition temperature \( |\Delta \tau| \). The solid line is Vogel-Fulcher times \( t \sim t_0 \exp(b_0/|\Delta \tau|) \); with \( t_0 = 3, b_0 = 3.3 \). Inset: Plot of \( 1/t \) versus \( |\Delta \tau| \) falls on a line to the origin. Compare Fig.9.

Figure 10: Experimental conversion-delay times: The measured conversion-delay times [15] \( t \) (in hours) versus deviation from transition temperature \( |\Delta \tau| \). The solid line is Vogel-Fulcher times \( t \sim t_0 \exp(b_0/|\Delta \tau|) \); with \( t_0 = 3, b_0 = 3.3 \). Inset: Plot of \( 1/t \) versus \( |\Delta \tau| \) falls on a line to the origin. Compare Fig.9.

In an experiment Abe et al [18] noted incubation times \( t_{1/2} \) when the martensite fraction \( X(t) = 1/2 \) at temperatures \( T_0 > T > M_t \), from X-ray diffraction. This is similar to (3.1) of conversion time \( t_m \) when martensite fraction \( n_m(t) = 1/2 \). We extracted incubation-times \( t \) from Abe et al [18] and plotted in Fig. 10 as \( t \), in hours, versus \( \Delta T = T - T_0 \). The incubation times shows Vogel-Fulcher behaviour \( t \sim t_0 \exp(b_0/|\Delta T|) \) as in simulations. The same data is plotted in inset of Fig.10 as \( 1/t \) versus \( |\Delta T| \) that shows linearity as \( |\Delta T| \to 0 \).

In principle one can relate experimental data [19] to the pseudospin model parameters [11, 14]. We need to measure, for a particular martensite, (i) the temperature-dependent elastic constants \( C_{11}(T), C_{12}(T), C_{44}(T) \) in the vicinity of the Landau transition \( T_0 \) from sound velocities; (ii) from combination of elastic constants, \( C(T) = C_{11} - C_{22} = (T - T_c)C_0(5) \), of linear slopes \( C_0(5) \) and the extrapolated softening temperature \( T_c \) (which is preempted by first-order transition \( T_0 \)); (iii) the jump \( \lambda \) in the OP strain magnitude at \( T_0 \) from X-ray data of elastic constants; (iv) and long-wavelength curvatures \( b \) from phonon dispersion curves. The dimensionless parameters \( A_1, E_0, \xi^2 \) are [14]

\[ A_1 = [C_{11}(T_0) + 2C_{12}(T_0)]/\lambda C(T_0), \] \[ \xi^2 = b/[C(T_0)C_0^2]. \]
Figure 12: Evolution for the Triangle-centered rectangle (TCR) transition: First row: Snapshots of OP strain $\mathbf{S}$ for different times $t$ on quenching to $\tau = -2.7$. See movie of this evolution. The color bar represents variant label $V$. See text. Second row: Evolving stress distributions of $p_2(\mathbf{r})$, $p_3(\mathbf{r})$. Parameters: $A_1 = 4$, $E_0 = 3$.

Figure 13: Evolution for the Square-oblique (SO) transition: First row: Snapshots versus time $t$, of OP strain $\mathbf{S} = (S_2, S_3)$ on quenching to $\tau = -1.1$. The colour bar is in terms of variant label $V$. See movie. Second row: Evolving stress distributions $p_2(\mathbf{r})$, $p_3(\mathbf{r})$. Parameters: $A_1 = 4$, $E_0 = 3$.

Figure 14: Evolution for the Triangle-oblique (TO) transition: First row: Snapshots of the OP strain $\mathbf{S} = (S_2, S_3)$ evolution in terms of $V$ on quenching to $\tau = -1.1$. See movie. Second row: Stress distributions $p_2(\mathbf{r})$, $p_3(\mathbf{r})$. Parameters: $A_1 = 4$, $E_0 = 3$. 
Here, $k_B$ is the Boltzmann constant and $a_0$ is the smallest scale for an elastic constant description.

Figure 11 shows the TTT phase diagram in conversion times $t_m$ versus scaled variable $\eta(\tau) = -1/R_c(\tau)$ for fixed $A_1 = 4$, $E_0 = 3$ for TCR, SO, and TO transitions. The characteristic temperatures $\tau_{1,2,4}$ are defined as $\tau = \tau_1$ or $\eta(\tau) = -2$ where $t_m = 1$ MCS; $\tau = \tau_2$ or $\eta(\tau) = -1$ where $t_m = 10$ MCS; and $\tau = \tau_4$ or $\eta(\tau) = -0.5$, where conversion time diverges.

6. Evolution of textures

In the athermal parameter regime, after quenching into $\tau_4 > \tau > \tau_2$, we monitor evolution of OP strain $\mathbf{S}$ textures, local internal stresses (see Appendix), and stress distributions to understand the conversion-incubations at microstructural level. The color bar in Figs 12, 13, 14, 15 represents the OP strain $\mathbf{S}$ in terms of variant label $V$. In all the three transitions, $V = 0$ represents austenite $\mathbf{S} = 0$ and $V = 1, 2, ..., N_v$ corresponds to $N_v$ martensite variants with pseudospin vector values given in (2.14), and pictured in Fig 1.

As shown in Figs. 12, 13, 14 (first row), after quenching the austenite with 2% martensite seeds into $\tau_4 > \tau > \tau_2$, the seeds quickly form domain-wall ‘vapour’ of droplets of single variant(s), reminding of Ostwald ripening. The droplets searches for the rare pathway channels to expand in the easy directions of the anisotropic potential. The expanded droplet then generates the other variant by elastic photocopying [7, 11] to form ‘liquid’ of domain-walls, which orient to form domain-wall ‘crystal’ at a later time. The jerksiness during conversion incubation is reflected in wavenumber $k_m$ (not shown) as steps with finite values [14, 20] and also in (excess) thermodynamic quantities [14, 20], internal energy $DU$ and entropy $-TAS$ (not shown).

In the second row of Figs. 12, 13, 14, the local stress distributions $p_2(\mathbf{r}), p_3(\mathbf{r})$ are shown. At $t = 0$, the stress distributions are sharply peaked around zero with large values, which generate wings on both sides of the peak during elastic photocopying [7, 11]. In the final oriented state, only the wings remain that correspond to the trapped stress values along the domain-walls (except in TO case, where $p_3(\mathbf{r})$ is sharply peaked around zero).

The final ‘equilibrium’ microstructures in the TTT phase diagram for TCR, SO, and TO transitions are shown in Figure 15 and are in good agreement with the continuous variable simulations and experiments [5, 6, 7].

With random initial seeds, there is a vibrating martensite phase that has bulk austenite in TCR, SO, and TO transitions as in Fig.15(a) that could be equivalent of chequerboard SR case (not shown) (and becomes less probable closer to $\tau_4$).

With 2% of martensite seeds, and for $\tau > \tau_4$ or $\eta(\tau) > -0.5$, there is only uniform austenite. For $\tau_2 \lesssim \tau \lesssim \tau_4$ or $-1 \lesssim \eta \lesssim -0.5$, there are again austenite droplets but now appear as lines, in domain wall crystal (DWC) in SO, TO cases, and Z-like states [10] in TCR case as in Fig.15 (b). For $\tau_1 \lesssim \tau < \tau_2$ or $-2 \lesssim \eta(\tau) < -1$, austenite droplets can appear as points at corners, in DWC (that have topological charges) in SO, TO cases; and also fan-like oriented states [10] in TCR case as shown in Fig.15 (c).

7. Conversions without the Compatibility interaction

We now turn-off the compatibility term ($A_1 = 0$) in the Hamiltonians for TCR, SO and TO transitions to understand the role of the power-law anisotropic potentials.

Figure 16 showing the martensite fraction $n_m(t)$ versus time $t$ for various $|\Delta \tau| = |\tau - \tau_4|$, where $\tau_4$ is austenite transition temperature; and conversion times $t_m$ versus $\Delta \tau$ for different $E_0$ for TCR, SO, and TO transitions with stiffness $A_1 = 0$. Here, $n_m$ has no flat regions or incubation as was seen for $A_1 = 4$ in Fig.5. The final microstructure is a slab-like martensite unlike oriented microstructures in $A_1 = 4$ as in Fig.15. Conversion times show a rise at $\tau_1$ that almost remains constant till $\tau_2$ and then increase linearly to $\tau_4$, above which there are no conversions found. There are no Vogel-Fulcher rises in conversions as in $A_1 = 4$ (Fig.9), but there is a small $E_0$ dependence, which could be now from energy barriers rather than entropy barriers.

With the parametrization scale of (4.2) now given by $R(\tau_{1}) = 2E_0^2/|g_1|$, the estimated transition temperatures are $\tau_1 = -5.5, -4.0, -4.0$; $\tau_2 = -2.0, -1.4, -1.4$; $\tau_4 = -0.4, -0.2, -0.2$ are in good agreement with the simulation values of $\tau_1 = E_0 = C(T_0)\lambda^2 a_0^3/k_BT_0. \quad (5.1c)$
$-5.5, -4.0, -4.0; \tau_2 = -2.0, -1.4, -1.4; \tau_4 \approx -0.8, -0.1, -0.1$ for TCR, SO, and TO transitions respectively.

Therefore, microstructures and conversion times in TCR, SO, and TO transitions with $A_1 = 0$ are clearly different from the non-zero $A_1$ case. Thus, the power-law anisotropic potentials in ferroelastic transitions are important in understanding orientations and kinetics of domain-walls.

8. Summary and further work

Systematic temperature-quench MC simulations without extrinsic disorder are carried out on the strain pseudospin clock-zero model Hamiltonians, with vector-order parameter ($N_{OF} = 2$) and $N_e + 1(= 4, 5, 7)$ strain-pseudospins that correspond to triangle-to-centred rectangle, square-to-oblique, and triangle-to-oblique transitions to get insights into conversion-incubation kinetics. The results are similar to the SR case [14] that are just seen to be generic. The simulation results are as follows:

1) The microstructures of discrete-strain pseudospins in the Temperature-Time-Transformation diagram are in good agreement with continuous-variable simulations and experiment.

2) On quenching, martensite fraction $n_m(t)$ can have slow isothermal and fast athermal conversions for different material parameters $T_c/T_0, \xi^2, A_1, E_0$. The conversion times $\bar{t}_m$ can transform from rapid athermal to slow isothermal or vice versa on changing the material parameters; and athermal/isothermal/austenite regime diagrams are obtained.

3) Focusing on the athermal parameter regime, we find rapid conversions below a spinodal-like temperature and incubation delay above it, as in the experiment. The conversion-delay times have Vogel-Fulcher divergences, which are insensitive to Hamiltonian energy scales $E_0$ from entropy barriers.

4) The athermal parameter regime crossover temperatures in the TTT phase diagram are understood through parametrization of domain wall textures by surrogate droplet energies.

5) During conversion incubation ($t_m$), evolutions of microstructures, stress distributions and domain-wall thermodynamics are monitored. The initial martensite seeds in the austenite at $t = 0$ disappear to form a domain-wall vapour of single variant droplet(s) that incubates before generating $N_e$ variants, one after the other, by elastic photocopying [7, 11] to convert to domain-wall liquid. The wandering domain-walls then orient later to a domain-wall crystal. During incubation, stress distributions remain sharply peaked, and there are finite steps in (excess) internal energy, (excess) entropy.

6) On switching off the power-law anisotropic potentials, we find no incubations in conversions, no Vogel-Fulcher divergences and the microstructure is multi-slab martensite.

Systematic experiments on athermal martensites can look for martensite formation and growth during conversion incubation and their divergences close to the transition.

Monte Carlo simulations presented in this paper are on 2D strain-pseudospin models for ferroelastic transitions with vector-OP. We also find similar conversion incubation-delays in 3D strain-pseudospin models for tetragonal-to-orthorhombic ($N_e = 2, N_{OF} = 1$), cubic-to-tetragonal ($N_e = 3, N_{OF} = 2$), cubic-to-orthorhombic ($N_e = 6, N_{OF} = 2$), and cubic-trigonal ($N_e = 4, N_{OF} = 3$) ferroelastic transitions [21].

Acknowledgements: It is a pleasure to thank S.R. Shenoy, T. Lookman and K.P.N. Murthy for very helpful discussions, and S.R. Shenoy for help with the manuscript. The UGC-India is thanked for Dr. D.S. Kothari Postdoctoral Fellowship.

APPENDIX: internal stresses

The local internal stresses, $p_2(r) = \partial \bar{F} / \partial \xi_2(\bar{r})$, and $p_3(r) = \partial \bar{F} / \partial \xi_3(\bar{r})$ for TCR transition are obtained as,

\[ p_2(r) = \left[ 4e^2S_2^3 - 6eS_2^4 + 2S_2(2e^2S_2^2 + \tau) + 6eS_3^2 + 2e\xi^2\Delta S_2 + A_1(U_{23}S_2 + U_{33}S_3) \right]. \quad (A.1a) \]

\[ p_3(r) = \left[ 4e^2S_2^3 + 2S_3(2e^2S_2^2 + 6eS_2^3 + \tau) + 2e^2\xi^2\Delta S_3 + A_1(U_{23}S_2 + U_{33}S_3) \right]. \quad (A.1b) \]

The local internal stresses for SO transition are,

\[ p_2(r) = \left[ 2S_2(3S_2^3 - 4S_2^5 + \tau) + 2e^2\xi^2\Delta S_2 + A_1(U_{23}S_2 + U_{33}S_3) \right]. \quad (A.2a) \]

\[ p_3(r) = \left[ 2S_3(3S_3^3 - 4S_3^5 + \tau) + 2e^2\xi^2\Delta S_3 + A_1(U_{23}S_2 + U_{33}S_3) \right]. \quad (A.2b) \]
The local internal stresses for TO transition are,

\[ p_2(r) = \epsilon [2S_2(3S_2^4 - 4S_2^2 + \tau) + 2\xi^2\Delta^2 S_2] \]
\[ + A_1 (U_{22}S_2 + U_{33}S_3), \quad (A.3a) \]

\[ p_3(r) = \epsilon [2S_2(3S_3^4 - 4S_3^2 + \tau) + 2\xi^2\Delta^2 S_3] \]
\[ + A_1 (U_{22}S_2 + U_{33}S_3), \quad (A.3b) \]

[1] K. Bhattacharya, Microstructure of Martensite, Oxford University Press, Oxford (2003); [2] Physical properties of martensite and bainite, Proceedings of the joint conference organized by the British Iron and Steel Research Association and the Iron and Steel Institute, Special report 93, London (1965).