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Conversion times and energy/entropy barriers in isothermal/athermal martensites

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ABSTRACT

We obtain insights into the athermal/isothermal martensite classification, and into puzzling delay times in athermal martensites, from Monte Carlo temperature-quench simulations of a discrete-strain pseudospin model for a square to rectangle transition.

1. Introduction

Many functional materials such as martensitic steels and shape memory alloys, high temperature superconductors and colossal magnetoresistance manganites, undergo ferroelastic structural transitions, with components of the spontaneous strain tensor as the order parameter [1–6]. Competing variants with different low-temperature unit cells, can coexist in different regions separated by strain domain walls, such as twins oriented along preferred crystallographic directions. This elastic texturing can be described by local distortion matrices acting on the reference lattice vectors [4]; by phase fields that describe the local unit cell phases [7]; or by Ginzburg–Landau free energies as invariant polynomials of the local physical strains [8–10].

Martensites have for decades, been classified as isothermal or athermal, with respectively slow or fast conversion from austenite [1–3]. In a more recent puzzle, an athermal material quenched to above its martensite start temperature M_s (where there should only be austenite), has been shown to convert to martensite after a delay, that is longer for higher temperatures [11]. Other athermal materials show no such conversion even after annealing at $T > M_s$ for 21 days [12]. The temperature-dependent delay tail has been modelled by temperature-dependent Landau metastability barriers to austenite conversion, that decrease and vanish at a spinodal temperature $\sim M_s$ [13]. These three results need to be reconciled [14].

In this paper, we present an overview as well as new results on a discrete-strain [15], or pseudospin version of the Ginzburg–Landau strain approach [16,17]. Monte Carlo simulations [18] of such pseudospin Hamiltonians yield insights into both long-standing and recent issues in athermal and isothermal martensites [1–3,11–13].

The physical strains $\{e_i\}$ are linear combinations of the components of the Cartesian strain tensor **e**, and in three dimensions we have 6 of them: one compressional or dilatational strain e_1; two deviatoric or rectangular strains e_2, e_3; and three shear strains e_4, e_5, e_6. To understand complex martensitic transition, it makes sense to initially consider the simplest, square-to-rectangle structural transition, that is a 2D '$x-y$' plane or [1 0 0] version of the 3D tetragonal-to- orthorhombic transition [8,9]. In two dimensions, there are 3 physical strains, namely one each of compressional e_1, deviatoric e_2 and shear e_6 strains. In the same spirit of simplicity, we exclude extrinsic disorder, that could be added later, considering only spontaneous nucleation. The order parameter (OP) then has one component $N_{OP} = 1$, and is the local deviatoric strain $e_2(\vec{r})$. As the free energy is invariant with respect to global rotations, and not just local point group symmetries, it will depend on Lagrangian-strain tensor **E** [19]. The Lagrangian-strains physical components $E_i = e_i + g_i$, are the physical strains e_i plus a geometric nonlinearity

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that is quadratic in the strains and local rotations. If all strains are scaled in the spontaneous strain at transition, that is typically a few percent, the quadratic corrections can be neglected, and $E_i \simeq e_i$, for scaled variables. The variational free energy F for a first-order transition then has a sixth order Landau free energy term $F_L(e_2) \sim e_2^6$ with three turning points: one at $e_2 = 0$ square unit-cell austenite, and martensitic variants $N_V = 2$, at positive and negative values of e_2. The elastic cost of a domain wall is a quadratic-gradient Ginzburg term, $F_G \sim (\vec{\Delta} e_2(\vec{r}))^2$. And finally, the non-order parameter costs are spring-like harmonic terms $F_{non} \sim e_1^2, e_6^2$. We need to minimize the total free energy $F(e_2; e_1, e_6) = F_L + F_G + F_{\rm non}$ to find textural local minima.

At first sight, the parabolic minima are where the non-OP strains are separately $e_1 = e_6 = 0$ at given OP e_2. However this implies all three physical strains are independent, while in 2D there must be only two independent displacement degrees of freedom per lattice point (or per unit cell). There must be one constraint in 2D linking the three strains, so in the end there are also two independent strain variables. The needed constraint is the St Venant compatibility condition [8,9]. This double-Curl constraint on the Cartesian-component strain tensor, $\vec{\Delta} \times (\vec{\Delta} \times \mathbf{e})^T = \mathbf{0}$, where '$T$' is a transpose, is satisfied as an identity when writing strains as displacement gradients. (It is analogous to the $\vec{\Delta}.\vec{B} = 0$ Maxwell equation reducing to an identity, when the magnetic induction is written as the Curl of a vector potential.) The St Venant compatibility constraint has at all times, a zero source term on the right (zero Burger's vector), and it says that spontaneously-distorted unit cells fit together in a smoothly compatible way, with no generation of defects like dislocations, on cooling. In 3D, with 6 physical strains, there are 3 distinct constraints, so in the end there are 3 independent strain variables, as there must be.

The St Venant condition can be written in terms of physical strains e_2, e_1, e_6, and links them, so a constrained minimisation in Fourier space of $F_{\rm non}(e_1, e_6)$ yields non-OP strains e_1, e_6 in terms of the OP e_2 [8,9,16]. Substitution back yields a nonlocal effective OP–OP interaction $F_{\rm non} \to F(e_2)$, that turns out to have a power-law anisotropic potential $U(\vec{r} - \vec{r}') \sim \cos 4(\theta - \theta')/|\vec{r} - \vec{r}'|^d$, where the anisotropy factor reflects the four-fold symmetry of the square unit cell, and the fall-off exponent is the dimensionality: $d = 2$. A ferroelastic transition with a group-subgroup symmetry change, has $N_{\rm OP}$ order parameters as a vector $\vec{e}$ in OP space, with a Landau free energy $F(\vec{e})$ having N_V martensitic-variant minima. Each transition has its own characteristic Fourier-space kernel, that is an $N_{\rm OP} \times N_{\rm OP}$ matrix $\mathbf{U}(\vec{k})$. These have been evaluated [16] for the square/rectangle transition ($N_{\rm OP} = 1, N_V = 2$) and all other transitions in 2D; and in 3D for the tetragonal/ orthorhombic ($N_{\rm OP} = 1, N_V = 2$); cubic/ tetragonal ($N_{\rm OP} = 2$, $N_V = 3$); cubic/orthorhombic ($N_{\rm OP} = 2$, $N_V = 6$); and cubic/ trigonal ($N_{\rm OP} = 3, N_V = 4$), transitions [16].

In general, the nonlinear Landau free energy has many higher-order elastic coefficients of the OP strain powers, that are difficult to extract from experiment. The most accessible is the quadratic-term coefficient or elastic constant $C'(T) \sim C_{11} - C_{12} \sim (T - T_c)A_{20}$, whose softening to zero at a T_c with a slope A_{20}, is pre-empted by a first-order transition at a temperature $T_0 > T_c$. Following Barsch and Krumhansl [6], physical strains $\{e_i\}$ are scaled in the jump λ of the spontaneous-strain magnitude $|\vec{e}|$ at $T = T_0$ the austenite/martensite free energy crossing, while Landau polynomial term is scaled in an energy-per-unit-cell E_0. It turns out that the parameters E_0, λ, T_0, can be chosen [16] such that higher-order elastic coefficients are absorbed into an overall E_0 prefactor, and into an internal prefactor λ of the geometrical nonlinearities. Thus with $e_i \to \lambda e_i$, $E_i \to \lambda(e_i + \lambda g_i)$, the geometric nonlinearities can be neglected for $\lambda << 1$, so $E_i \simeq e_i$, as mentioned. Thus one has 'quasi-universality' [16], with a material-independent $F_L(\vec{e})/E_0$. The scaled N_V free energy minima in OP space then fall on the corners of polygons inscribed in a sphere, of temperature-dependent radius $|\vec{e}| = \bar{\varepsilon}(\tau)$ that is unity at transition. The coefficient of the scaled quadratic term $F_L \sim \tau\ \vec{e}^2$ defines a dimensionless temperature variable used throughout,

$$\tau(T) = (T - T_c)/(T_0 - T_c),$$

that is unity at transition $T = T_0$, and vanishes at $T = T_c < T_0$, when the austenite minimum disappears. Clearly $\tau(T) > \tau_0$ where $\tau_0 \equiv \tau(T = 0) = -T_c/(T_0 - T_c)$. The temperature T in terms of τ is $T = T_c[1 - \tau/\tau_0]$.

Evolving textures can be studied using $F(\vec{e})$, through numerical solutions of the underdamped strain dynamics [8–10]. Since differential equations with nonlinear terms can be time-consuming, we seek a reduced model description. This emerges naturally from the scaled free energy minima on an OP sphere. Discrete-strain variables, or 'pseudospins', are defined by the scaled-strains OP vector pointing to minima $\vec{e}(\vec{r}) \to \bar{\varepsilon}(\tau)\vec{S}(\vec{r})$, where $\vec{S}^2 = 1$ for variants, and $\vec{S} = \vec{0}$ at the austenite turning point. The pseudospin hamiltonian is simply the free energy evaluated at these turning points $H(\vec{S}) = F(\vec{e} \to \bar{\varepsilon}(\tau)\vec{S})$. The nonlinearities collapse, as $\vec{S}^6 = \vec{S}^4 = \vec{S}^2 = 0, 1$, and so $F_L \sim \vec{S}^2$. The hamiltonian is then bilinear in the pseudospins, as in clock models, but here with powerlaw interactions and temperature dependence, inherited from the free energy [16]. The statistical methods familiar in spin models can then be applied to elasticity problems, including (local) meanfield approximations, and Monte Carlo simulations [17,18].

For the square/ rectangle transition with $N_{OP} = 1$, $N_V = 2$, or a scalar, three-valued $S = 0, \pm 1$, the hamiltonian on a square grid of unit lattice constant is, in Fourier space ($\beta = 1/k_BT$),

$$\beta H = \frac{1}{2}\sum_{\vec{k}} Q_0(\vec{k})|S(\vec{k})|^2,$$

where $Q_0(\vec{k}) = D_0[g_L(\tau) + \xi^2\vec{K}^2 + \frac{1}{2}A_1U(\vec{k})]$; $D_0 \equiv 2E_0\bar{\varepsilon}^2/k_BT$; $g_L \equiv (\tau - 1) + (\bar{\varepsilon}^2 - 1)^2 < 0$ for $T < T_0$; and $\bar{\varepsilon}^2 = (2/3)(1 + \sqrt{1 - 3\tau/4})$. The Landau free energy density at minima is $f_L = \bar{\varepsilon}^2 g_L$. Here A_1 is a scaled dimensionless elastic constant at transition $\sim C_{11}(T_0)/C'(T_0)$, related to the anisotropy parameter.

Every structural transition has its own specific kernel, that for the square/ rectangle case is $\nu = 1 - \delta_{\vec{k},0}$

$$U(\vec{k}) = \nu(\vec{k})(K_x^2 - K_y^2)^2/[K^4 + (8A_1/A_3)(K_xK_y)^2].$$

where on a unit grid, $K_\mu = 2\sin(k_\mu/2)$.

In coordinate space, the hamiltonian is

$$\beta H = \frac{D_0}{2}\left[\sum_{\vec{r}}\{g_L(\tau)S(\vec{r})^2 + \xi^2(\vec{\Delta}S)^2\} + \sum_{\vec{r},\vec{r}'}\frac{A_1}{2}U(\vec{r} - \vec{r}')S(\vec{r})S(\vec{r}')\right].$$

Typical parameter values are $\xi^2 = 1$; $E_0/k_BT_0 = 3, 4, 5, 6$; $T_c/T_0 = 0.5 - 0.95$. Henceforth, dimensionless variables are used, with E_0 and T scaled in k_BT_0 and T_0 respectively. A single Monte Carlo sweep is completed when all of $N = L^2$ sites are visited once and only once, so 1 MC sweep corresponds to 1 Monte Carlo step per spin. The temperature is quenched to a constant value τ and held for a holding time $t = t_h$ sweeps, with $t_h < 20,000$. The initial state $\{S(\vec{r}, 0)\}$ has square seeds in an austenite sea, of geometric side $R(0) = 1, 2, 3\ldots$ and initial martensite fraction $n_m(0) = 0.02$ or 2%. The evolution of $\{S(\vec{r}, t)\}$ is monitored. The martensite conversion time t_m is when $n_m(t) = \sum_{\vec{r}} S^2(\vec{r}, t)$ rises to a specified value, that we take as 50% conversion, or $n_m(t_m) = 0.5$. This rise is found to be sigmoidal for small stiffness/anisotropy $A_1 < 1$. For $A_1 > 1$ it is flat with step-like early bursts at short times $t << t_m$ where $n_m(t) << 1$, followed by sharp rises to unity at longer times $t \sim t_m$ [18].

Fig. 1 shows that martensite droplet formation in one region can induce spreading droplets in other regions, as noted in the