Hysteresis and Power-Law Statistics during temperature induced martensitic transformation

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Abstract. We study hysteresis in temperature induced martensitic transformation using a 2D model solid exhibiting a square to rhombic structural transition. We find that upon quenching, the high temperature square phase, martensites are nucleated at sites having large non-affineness and ultimately invades the whole of the high temperature square phase. On heating the martensite, the high temperature square phase is restored. The transformation proceeds through avalanches. The amplitude and the time-duration of these avalanches exhibit power-law statistics both during heating and cooling of the system. The exponents corresponding to heating and cooling are different thereby indicating that the nucleation and dissolution of the product phase follows different transformation mechanism.

1. Introduction

As a direct consequence of breaking of translational and orientational symmetry, a solid, with a fixed composition, can exist in several forms with distinct crystallographic symmetries. Changing thermodynamic parameters like temperature, pressure, external stress, magnetic or electric fields [1, 2, 3, 4, 5], one can cause transitions between these structures. These transitions can be either continuous, appearing due to mechanical instabilities in the solid, or first order, when both the parent and the product phases are locally stable [6]. The transformation in this case proceeds via nucleation and growth [7]. Unlike most kinds of phase transitions, solids, however, rarely go to equilibrium [8] following a quench across a structural transition, often getting arrested in long lived metastable states called “microstructures” [9]. Most microstructures are crystalline over short length scales but lack long range order beyond some characteristic length set by the presence of defects like dislocations, grain boundaries etc. The final microstructure is determined by, among other things, depth of quench rate and transformation protocol [9]. For example, transformations at high temperatures are generally accompanied by large scale rearrangements of atomic positions where elasticity plays a relatively minor role in determining the final microstructure [8, 9, 10]. On the other hand, at low temperatures, the large scale structure is mainly determined by elasticity [8, 9]. This is especially true when the parent and product solids are crystallographically “incompatible” giving rise to interfacial strain across a parent-product interface [11]. How this strain is accommodated then determines, to a large
extent, the microstructures.
In this work, we look into the dynamics of microstructures during a temperature induced martensitic transformation in a model 2D solid exhibiting a square to rhombic structural transition. The system is gradually cooled from a high temperature square phase resulting in complex twinned microstructures. The product phase nucleates at sites determined by a large non-affineness. On heating the microstructure, we recover the initial square phase. The dissipation during the transition follows a power-law statistics both during heating and cooling with different exponents.

In section 2, we revisit elasto-plastic theory [13]. Starting from a basic Lagrangian and motivated by the molecular dynamics study of the model system [12], we derive dynamical equations for the relevant variables. Section 3 deals with the procedure undertaken to manifest temperature-induced martensites and the analysis of the results concerning microstructure evolution and the statistics of dissipation during the transition. Lastly in section 4, we discuss our results and outline possible future work within the framework of elasto-plastic theory.

2. The model
In this section we revisit our Elasto-plastic continuum theory [12, 13] for structural transitions in solids. Our theory allows us to determine the microstructure and the overall shape of a solid undergoing a square to a general oblique lattice. Unlike previous work in this subject [14, 15] we allow for the presence of non-affine, or plastic deformations [12, 13].

We assume that the components of the strain tensor e may be additively decomposed into elastic (affine) and plastic parts [17], viz. \( e_{ij} = e_{ij}^A + e_{ij}^P \) where \( i, j = x, y \). The plastic strains \( e_{ij}^P \) represents the total contribution from space and time dependent displacements which cannot be derived from an affine deformation. Such displacements may or may not be associated with individual microscopic defects, which, in the spirit of our continuum approach, need not be resolved into individual, microscopic defects. Non-affineness introduces multivaluedness in the particle displacement field \( u = (u_x(r), u_y(r)) \) and cause the elastic parts of the strain to violate the St. Venant’s compatibility condition [18], viz.

\[
\nabla \times (\nabla \times e)^T = 0
\]

Note that this implies that the total strain tensor \( e \), nevertheless, does satisfy the compatibility condition.

The structural transition is driven by the non-linear response of the solid to one or more components of the strain - the order parameter (OP). For example, for the \((p4mm \rightarrow p2)\) transition, the order parameter strains are \( e_2 = e_{xx} - e_{yy} \) and \( e_3 = e_{xy} + e_{yx} \) while the remaining volumetric strain \( e_1^A = e_{xx} + e_{yy} \) is a non-order parameter (NOP) strain [19]. We shall only consider the case when plasticity exists in the NOP sector.

The transition is described by the following free energy functional:

\[
\mathcal{F} = \frac{1}{2} \int dy \left[ a_1(e_1^A + e_1^P)^2 + a_2 e_2^2 + a_3 e_3^2 - \frac{1}{2} b_3 e_3^4 \right] + \frac{1}{3} d_3 e_3^6 + c_1(\nabla e_1^A)^2 + c_2(\nabla e_2)^2 + c_3(\nabla e_3)^2
\]

In Eqn.2 we have made the simplifying assumption that the product oblique lattice is actually a rhombus so that the equilibrium value of \( e_2 = 0 \). This choice is motivated by MD simulation of our particular model solid[12] though we do not doubt that our theory may be easily extended to the general case. The three elastic constants \( a_1, a_2 \) and \( a_3 \) define the linear elasticity of the square (parent) phase. The connection with external control parameters such as temperature (\( T \)) is,
Figure 1. The homogeneous part of the free energy functional $\mathcal{F}(e_3)$ as a function of the OP strain $e_3$ for different values of the parameters $a_3$ and the external stress $\sigma_3^{\text{ext}}$ viz. $a_3 = 0.5, \sigma_3^{\text{ext}} = 0$ (I), $a_3 = 0.1, \sigma_3^{\text{ext}} = 0$ (II) and $a_3 = 0.1, \sigma_3^{\text{ext}} = .1$ (III). The rest of the parameters $b_3 = -1$ and $d_3 = 1$ throughout. Inset shows a schematic representation of the typical dynamics of plastic strain $\dot{e}_i^P$ as a function of the local stress $\sigma_i$ used in our calculations. Similar dynamics is assumed for volumetric (NOP, $i = 1$) as well as shear (OP, $i = 3$) plasticity. The threshold stress $\sigma_i^c$ is, of course, different in the two cases.

as usual, through the temperature dependence of these coefficients especially $a_3 \propto (T - T^*)/T^*$ where $T^*$ is the limit of stability of the square solid. Reducing $a_3$ by cooling the solid stabilizes the rhombic phase (see Fig.1). The rest of the coefficients parametrize non-linearities and may be taken to be constants.

The Lagrangian is given by [15],

$$\mathcal{L} = \int \frac{\rho}{2} \left[ (\dot{u}_x^2 + \dot{u}_y^2) \right] dxdy - \mathcal{F}$$

(3)

To obtain the equation of motion in the displacement fields, we need to solve the Euler Lagrange equation given by Eqn.4.

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{u}_i} - \frac{\partial \mathcal{L}}{\partial u_i} = -\frac{\partial \mathcal{R}}{\partial \dot{u}_i}.$$  

(4)

The Rayleigh dissipation functional [16] is given by $\mathcal{R} = \frac{1}{2} \int \left[ \gamma_1 (\dot{e}_A^1)^2 + \gamma_2 \dot{e}_2^2 + \gamma_3 \dot{e}_3^2 \right] dxdy$, where the coefficients $\gamma_1, \gamma_2$ and $\gamma_3$ are the corresponding viscosity coefficients of the system.

Since there is symmetry breaking in the space of the OP strains, the dynamics of $e_2$ and $e_3$ – the broken symmetry variables – is much slower than that of the affine NOP strain $e_1^A$. Therefore $e_1^A$ reaches a steady state much faster compared to $e_2$ and $e_3$ and we can simplify by assuming that $e_1^A$ is slaved, at all times, to the OP strains $e_2$ and $e_3$. Also note that, the St. Venant’s compatibility condition (Eqn.1) may be used to eliminate $e_2$. Taking note of the above arguments and using Eqns.2, 3 and 4, we obtain the following equations of motion for the affine strains $e_1, e_2$ and $e_3$:

$$\nabla^2 e_1^A = 2 \left( \frac{a_2 - a_3}{a_1 + a_2} \right) \frac{\partial^2 e_3}{\partial x \partial y} - \nabla^2 e_1^P,$$  

(5)

$$\rho \ddot{e}_3 = \nabla^2 \left( \frac{\delta \mathcal{F}}{\delta e_3} + \frac{\delta \mathcal{R}}{\delta e_3} \right) + 2 \frac{\partial^2}{\partial x \partial y} \left( \frac{\delta \mathcal{F}}{\delta e_1^A} + \frac{\delta \mathcal{R}}{\delta e_1^A} \right).$$  

(6)

Lastly, the dynamics of the plastic strain $e_1^P$ needs to be specified. We assume that this is
given by the following simple phenomenological equation of motion used by us (Fig.1 inset) is,

\[ \dot{e}_1^P = - \frac{1}{h_1} \sigma_1 + c_p \nabla^2 e_1^P \quad \text{if } |\sigma_1| > \sigma_{1c} \]
\[ = c_p \nabla^2 e_1^P \quad \text{otherwise} \]

where \( \sigma_1 = a_1 e_1 \) is the volumetric stress, \( c_p \) is the diffusion coefficient in the plastic strain dynamics and \( h_1 \) is the viscosity. In reality, plastic strain production depends on the history of the system. Also defects once produced tends to reorganize themselves [23]. However, we have chosen not to incorporate any term(s) accounting for history dependence or defect reorganization in the plastic strain dynamics.

3. Temperature Induced Martensite
Martensitic transformations may be achieved by rapidly decreasing the temperature in the system (quenching) [20, 21]. In this work, we study the hysteresis behavior and microstructure evolution of martensites subjected to changes in temperature. Starting from an initial state with random \( e_1^P \) and a temperature, represented by the degree of undercooling \( a_3 \) and \( a_2 \), where the austenite (square) phase is the stable phase, the system is cooled from the austenite phase (\( e_3 = 0 \)) to the martensite phase (twinned rhombic) by simultaneously decreasing \( a_3 \) and \( a_2 \) from \( a_3 = a_2 = 3 \) to \( a_3 = a_2 = 0 \). We let the system evolve according to Eqn.5 to Eqn.6. We choose a simple dynamics for the plastic strain as in Eqn.7. After each temperature drop, the system is allowed to relax for a time interval of 20 units of time. Once the temperature reaches 0, the system is then heated back to the austenite phase (\( a_3 = a_2 = 3 \)) and a cycle of transformation is completed.

3.1. Hysteresis and Microstructure Evolution
Fig.2 shows the plot of the area fraction \( A \) occupied by martensitic phase as a function of the degree of undercooling \( a_3 \).

Figure 2. Plot of the area fraction \( A \) occupied by martensitic phase as a function of the degree of undercooling \( a_3 \).
Figure 3. Plot of $e_3$ profile and $e_{p1}$ profile with changes in the degree of undercooling $a_3$ for a system size of 256 $\times$ 256 during cooling. (a)(i) Microstructure for the austenite (square) phase. The red color indicates zero order parameter $e_3$.(ii) Initial random plastic strain $e_{p1}$. Colors ranging from $-500$ (black) to $500$ (yellow). (b)(i) Order parameter strain $e_3$ for degree of undercooling $a_3 = 1.8$. Colors ranging from $-1.5$ (black) to $1.5$ (yellow). Rhombic phase starts to appear at sporadic spatial locations indicated by dark yellow and dark blue colors. (ii) Plastic strain $e_{p1}$ for the same $a_3$. Colors range from $-4$ (black) to $2$ (yellow). The initial random plastic strain is now smoothened to a large extent. (c) $e_3$ for $a_3 = 1$. Colors ranging from $-1.5$ (black) to $1.5$ (yellow). Rhombic phases start to grow and traces of twinned microstructure is now visible. (ii) Plastic strain $e_{p1}$ for the same $a_3$. Colors range from $-4$ (black) to $5$ (yellow). (d)(i) $e_3$ for $a_3 = 0.2$. Colors ranging from $-1.5$ (black) to $1.5$ (yellow). The system has now completely transformed into the twinned martensite. (ii) The plastic strain $e_{p1}$ profile has not however undergone much change.

martensite finish temperature. However, on heating the system back to the austenite phase, the system retains its martensitic microstructure almost completely as far as a temperature of about $a_3 = a_2 = 1$, after which the martensites become unstable and the twinned microstructure slowly dissolves into the austenite phase. The transformation from the martensite to austenite is complete when the degree of undercooling reaches a value of about $2.4$. What is clearly evident from Fig.2 is that the martensites appear more rapidly and dissolve slowly.

The gradual evolution of martensitic microstructure with decrease in temperature is shown in Fig.3. We begin with an austenite (square) phase wherein the order parameter strain $e_3$ is zero everywhere and random plastic strain $e_{p1}$ is distributed throughout the system as shown in Fig.3(a)(i) & (ii). The system is then made to evolve according to Eqn.5, Eqn.6 and Eqn.7. Initially, the dynamics smoothens the profile of initial random $e_{p1}$ except at some arbitrary points in space which at later times act as the nucleation sites for the martensites [22]. This is evident in Fig.3(b)(ii). At this stage, product phases start to appear in the matrix of the austenite phase (Fig.3(b)(ii)). There are, however, no signs of twinned microstructure yet. The untwinned rhombic phases begin to grow in size on further decrease of temperature and traces of twinned martensite gradually appear as shown in Fig.3(c)(i). However, most of the system is still in the austenite (square) phase. Note that the new domains start forming at finite distances from each other. This is consistent with the autocatalytic nucleation mechanism known to occur in martensitic transitions [5, 22]. On decreasing the degree of undercooling $a_3$ to as low as 0.2, the austenite (square) phase transforms completely into martensites. The plastic strain profile (Fig.3(d)(ii)) however doesn’t undergo much noticeable change.

However, on gradual heating of the martensitic phase, the system retains the twinned microstructure for a large temperature regime before slowly transforming into the austenite (square) phase. The system first loses the twin structure as can be seen from Fig.4(a)(i). Plastic
strains are not produced anew anywhere because no new twins are formed that can account for large stresses at the twin boundaries required for plastic strain production. The plastic strain \( e_{1}^{p} \) gradually diffuses with time (see Fig.4(a)(ii)&(b)(ii)). Further increase of \( a_{3} \) to 2.44 leads to the transformation of the rhombic phase to the square phase almost completely. This is in accordance with the result shown in Fig.2 where the area-fraction is almost zero for \( a_{3} = 2.44 \). On heating the system more, there are no microstructural changes observed as can be seen from Fig.4(c)(i). The plastic strain has now diffused away completely (Fig.4(c)(ii)). Note that if the system is cooled again, it is now more difficult to nucleate martensites because most of the plastic strain, which facilitates nucleation, has diffused away (annealed). However, in real systems, martensites reappear if the system is cooled again. Our Elasto-plastic Theory fails to reproduce this feature because of the absence of the effect of defect reorganization and defect pinning in the plastic strain dynamics. In reality, defects would organize into grain boundaries which provide sites for martensite nucleation.

Figure 5. Typical plot of dissipation over a complete thermal cycling. The transformation from the high temperature austenite to the low temperature martensite phase proceeds through bursts of energy release.
3.2. Avalanches and Power Law Statistics

The transformation from the high temperature austenite phase to the low temperature martensite phase proceeds through dissipation of energy. The physical origin of this dissipation can be attributed to phonon viscosity, dislocation drag, electronic damping, frictional sliding of the twins, friction encountered by the growing product phase against the parent phase backdrop, etc. The signature of energy dissipation is captured by acoustic emission measurements in experiments. Measurement of amplitude and time-duration of avalanches in acoustic emission signals during martensitic transformations of single crystal Cu-Zn-Al under thermal cycling yields a power law [21].

A typical plot of dissipation obtained during thermal cycling from our Elasto-plastic Theory is presented in Fig.5. It can be seen in Fig.5 that the transformation proceeds through avalanches. The energy is released through bursts and thus is consistent with acoustic emission studies [21]. Initially, the transition advances through small amplitude avalanches. After some time, however, once the twins start forming and growing, the dissipation rises sharply. The largest peak corresponds to the time when the twins hit the system boundary after which the dissipation decreases sharply to almost zero. The most prominent contribution to the dissipation can hence be attributed to the growth and frictional sliding of the twins. Dissipation thus ceases when the twin reaches the boundary thereby terminating further growth of the twins. It nevertheless rises again when the martensite starts transforming into the austenite on heating.

Figure 6. The blue line represents a schematic diagram of the avalanches in dissipation. The time-duration $\Delta t$ of an avalanche is evaluated by locating two consecutive minima in $R$ and finding out the time-difference between these two minima as illustrated in the figure. The amplitude of the avalanche $R_A$ corresponding to $\Delta t$ is evaluated by averaging the difference in the maximum of $R$ and the two minima of $R$ (located at the two ends of $\Delta t$).

The occurrence of these avalanches en-route to transition needs to be characterized. We evaluated the amplitude and time duration of each avalanche during both cooling and heating. The time duration of avalanches is computed by numerically evaluating the time in-between two adjacent minima of $R$ in the dissipation plot of Fig.5. To calculate the amplitude of the avalanche $R_A$ corresponding to a time duration, say $\Delta t$, we find the average difference in the maximum of $R$ and the two minima of $R$ (located at the two ends of $\Delta t$) in $\Delta t$. The procedure for evaluating $R_A$ and $\Delta t$ is illustrated in a schematic diagram in Fig.6.

Fig.7(a) & (b) plots the logarithmic plot of the probability distribution of the amplitude and time duration of avalanches respectively during cooling. We have obtained data of these avalanches for 12 realizations of the initial state of the system. The distribution of amplitude $R_A$ of avalanches follows a power-law statistics - $P(R_A) \sim R_A^{-\alpha_R}$ where $\alpha_R = 1.3$ for almost three
Figure 7. (a) Logarithmic plot of the probability distribution of the amplitude of avalanches during cooling. It has a power-law behavior for almost three decades with an exponent of 1.3. (b) Logarithmic plot of the probability distribution of the time duration of avalanches during cooling. It has a power-law behavior for more than two decades with an exponent of 1.7. The straight lines are a fit to the data.

Figure 8. (a) Logarithmic plot of the probability distribution of the amplitude of avalanches during heating. It has a power-law behavior for more than two decades with an exponent of 1.6. (b) Logarithmic plot of the probability distribution of the time duration of avalanches during heating. It has a power-law behavior for more than two decades with an exponent of 2. The straight lines are a fit to the data.

Also the distribution of time duration $\Delta t$ of avalanches follows a power-law statistics $P(\Delta t) \sim \Delta t^{-\tau_R}$ where $\tau_R^c = 1.7$ for more than two decades. The exponents obtained during heating and cooling are however different. This is also experimentally observed [21, 24] in martensitic transformation, the reason generally attributed to different dissipative mechanism in the growth and shrinkage of domains. Fig.8(a) & (b) show the probability distributions of the amplitude and time duration of avalanches respectively during heating. Both the probabilities showcase a power law statistics for at least two decades with coefficients given by $\alpha_R^c = 1.6$ and $\tau_R^c = 2$ respectively. Experimentally observed [21, 24] values of the exponents during cooling and heating is respectively $\alpha_R^c = 3.2 \pm 0.2$, $\tau_R^c = 1.6 \pm 0.3$ and $\alpha_R^h = 3.0 \pm 0.2$, $\tau_R^h = 1.6 \pm 0.3$. The large discrepancy in $\alpha_R$’s obtained from experiments and our Elasto-plastic Theory may be because of the difference in spatial dimension of the two observations. The experiments were done in three dimensions whereas our model system is in two dimensions. Another reason for the discrepancy may be because of the way we characterize the amplitude and time-duration of avalanches. There is however reasonable agreement in the $\tau_R$’s.
4. Conclusion
We have explored martensitic transformation under a single transformation protocol - temperature induced martensitic transformation. The martensite phase nucleates at defect cites determined by the presence of large non-affine strain. The transformation proceeds through avalanches in energy dissipation. The amplitude and the time-duration of these avalanches follow a power law statistics with different exponents during heating and cooling in temperature induced transformation. We have also looked into the possibility of reversibility of the microscopic patterns of the OP strain produced during the transformation. Unfortunately, such a reversibility at the very smallest length scales do not exist in our model. The reason for this may be attributed to the very simple phenomenological dynamics (Eqn.7) that we have used. In reality, which contains contribution arising from defects, would tend to reorganize and form patterns of its own, over a somewhat larger timescale. These patterns will then be correlated with that of the OP strain since defects provide sites for nucleation of new martensite plates. A more detailed study involving such phenomena is planned for the future.

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