Partial Equilibration Scenario in 3D athermal martensites quenched below first-order transition temperatures

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To test a Partial Equilibration Scenario (PES) of Ritort and colleagues, we do Monte Carlo simulations of discretized-strain spin models, for four 3D martensitic structural transitions under quenches to a bath temperature \( T < T_0 \) below a first-order transition. The ageing system faces entropy barriers, in searches for energy-lowering passages between quasi-microcanonical energy shells. We confirm the PES signature of an exponential-tail distribution of intermittent heat releases to the bath, scaled in an effective temperature, that in our case, depends on the quench. When its inverse \( \beta_{eff}(T) \equiv 1/T_{eff}(T) \) vanishes below a `martensite start' temperature \( T_1 \) of avalanche conversions, then entropy barriers vanish. When this search temperature \( T_{eff}(T) \) vanishes, PES cooling is arrested, as entropy barriers diverge. We find a linear vanishing of \( T_{eff}(T) \sim T_d - T \), below a delay-divergence temperature \( T_d \) in between, \( T_1 < T_d < T_0 \). Martensitic conversion delays \( e^{1/T_{eff}} \sim e^{1/(T_d-T)} \) thus have Vogel-Fulcher-Tammann like divergences. Post-quench delay data extracted from simulations and athermal martensitic alloys, are both consistent with predictions.

We consider other systems with structural transitions and equilibration delays. Martensitic steel alloys, when quenched from high temperature parent austenite to low temperature martensite,¹⁰¹¹ show strain domain-wall patterns.¹² They can exhibit puzzling delays in conversion to martensite that increase rapidly with temperature: raising \( T \) to nearer transition by a few percent, can raise delays from 1 sec to \( 10^4 \) seconds.²⁵

We do Monte Carlo simulations of quenches in \( T \), of martensitic discretized-strain models in 3D. The model hamiltonians describe the elastic Domain Walls (DW) or mobile twin boundaries, of four 3D structural transitions, each with characteristic anisotropic Compatibility interactions between order-parameter strains.²¹²² The four transitions can occur in martensite-related functional materials, where OP strains will be coupled to the functionality variables. The transitions are tetragonal-orthorhombic (YBCO, superconductivity); cubic-tetragonal (FePd, shape memory); cubic-orthorhombic (BaTiO, ferroelectrics); cubic trigonal (La5SrMnO, colossal magnetoresistance).

Our 3D simulations yield post-quench evolutions as in 2D, passing through three Domain Wall (DW) states. At first there is a majority-austenite DW Vapour state of a martensite droplet in an austenite background. This converts to majority-martensite DW Liquid, of randomly wandering walls. Finally the DW Liquid orders to a DW Crystal microstructure, with the walls along preferred direction, as in parallel ‘twins’.

We focus on the conversion delays of the first evolution of DW Vapour \( \rightarrow \) DW Liquid, that corresponds to austenite to martensite conversions, or a rise of the martensite fraction \( n_m(t) \) from zero to unity. As in the earlier 2D case, a phase diagram in material parameters is obtained. In the ‘athermal’ martensite regime, there are curious ‘incubations’, or no apparent changes after a quench, terminated by sudden avalanche conversion. In this regime, we find three character-
istic temperatures, with $T_1 < T_d < T_0$. Here $T_0$ is the meanfield transition to uniform ordering.

Avalanche conversions in a single MC time step $t_m = 1$, occur for $T < T_1$, identified as the martensite start temperature.$^{10,11}$ $M_s = T_1$. Quenches into $T_1 < T < T_d$ show (postponed) avalanches$^{23}$ or incubation behaviour: the conversion fraction $n_m(t)$ remains flat at zero, until there is a jump up to unity a time $t = t_m(T)$. The incubation delay time $t_m(T)$ extends rapidly, on approaching a divergence temperature $T_d$. The physical picture for delays is of Vapour-droplet Fourier profile attempting entry to a negative-energy region of effective Hamiltonian spectra $\epsilon(\vec{k}, T) < 0$. The profile has to pass through a zero-energy $\vec{k}$-space contour at a bottleneck, like a Golf Hole edge.$^{28,31}$ This transit passage delay differs from the familiar critical slowing down from a divergent Order Parameter length. The $T$-dependent, anisotropic bottleneck shrinks on warming, with a topological shape change at $T_d$, that blocks entry, so entropy barriers diverge. The precursor,$^{14,15}$ region $T_d < T < T_0$, where 2D results suggest dynamic tweed$^{27}$ may be studied elsewhere.

We use generic equilibration scenario of Ritort and colleagues to analyze the statistics of the set of energy changes $\delta E$ from each MC step (usually used but not retained$^{22}$). These heat releases are recorded up to an aging time $t_w = t_m(T)$, so the effective temperature depends on the quench temperature, $T_{eff}(t_w) \rightarrow T_{eff}(T)$: non-stationary distributions become time independent. We confirm the signature PES exponential tail for all four transitions. We find the search temperature vanishes linearly $T_{eff}(T) \sim T_d - T$, driving an entropy barrier divergence at $T_d$. The martensite-conversion times are thus predicted to show glass-like VFT behaviour, $e^{1/T_{eff}(T)} \sim e^{1/(T_d - T)}$ here understood as an arrest of PES cooling. Such VFT behaviour, is extracted from simulation and experimental$^{10,12}$ data.

The plan of the paper is as follows. In Section II, we discuss the generic Partial Equilibration Scenario and our specific case of quenching across a phase transition. Section III describes for the four transitions in 3D, the discrete-strain clock-like spins and their $T$-dependent Hamiltonians. In Section IV we describe the MC simulations, with delay results from the phase space bottlenecks in Section V. Section VI shows that PES signatures are seen in all four transitions. Section VII shows that both 3D simulations and metallic alloy experiments exhibit VFT behaviour. Finally Section VIII is a summary.

Appendix A illustrates how a continuum double-well Landau free energy induces a $T$-dependent, Ising effective Hamiltonian. Appendix B obtains the athermal phase diagram for four transitions. Movies of post-quench DW evolutions are in Supplementary Material Video.$^{23}$

II. SCENARIO FOR POST-QUECH Equilibration:

How do systems re-equilibrate, after a temperature quench? Ritort and coworkers have suggested that if an equilibrium canonical ensemble in thermal contact with a heat bath suddenly has its bath quenched to a lower temperature $T$, then the system goes into an ageing ensemble$^{14,15}$ that has a quasi-microcanonical description of states of the system. There are sequential passages through decreasing-energy configurational shells, and intervening entropy barriers in the system-search for the new equilibrium. While delays from energy barriers are from attempts through activated jumps, to cross mountains, delays from entropy barriers are from attempts through constant-energy searches, to find rare channels going through or around, the mountains.$^{31}$

In this Section we i) outline (our understanding of) the generic Partial Equilibration Ensemble$^{14,15}$ or PES, and ii) state how this ageing scenario is applied to our specific case, that has quenches across phase transitions, and order parameter emergence from zero.

i) Generic PES for aging after quenches:

The PES for the equilibration process considers a system of energy $E$ in contact with a (larger) heat bath. A familiar textbook derivation$^{33}$ of the canonical ensemble, applies the microcanonical ensemble to the system plus heat bath, of constant total energy $E_{tot} = E + E_{bath}$. The total number of states is the product of the $\Omega(E)$ states of the system, and of the $\Omega_{bath}(E_{tot} - E)$ states of the bath.
cases. After a bath quench from initial to a final T by the Law inequality summed over all allowed system energies 0 < E < E_{tot}:

\[ \Omega_{tot}(E_{tot}) = \sum_{E} \Omega(E) \Omega_{bath}(E_{tot} - E). \]  

The system configurational entropy is \( S(E) = \ln \Omega(E) \), and the inverse effective temperature is \( \beta_{eff} \equiv 1/T_{eff} = dS(E)/dE \). Similarly, the inverse bath temperature is \( \beta_{bath} \equiv 1/T_{bath} = dS_{bath}/dE_{bath} \). The change in total entropy depends on the system energy change \( dE \) as

\[ dS_{tot} = \frac{dS(E)}{dE} dE + \frac{dS_{bath}}{dE_{bath}} dE_{bath} = [\beta_{eff} - \beta_{bath}]dE \geq 0 \]  

(2)

with the equality at equilibrium, when the system and bath temperatures are equal \( \beta_{eff} = \beta_{bath} \). The Second Law inequality \( dS_{tot} > 0 \) must hold, for the irreversible cases. After a bath quench from initial to a final \( T_{bath} = T \), the system is left hotter, \( T_{eff} > T \), or \( \beta_{eff} - \beta_{bath} < 0 \). The energy changes are negative \( dE = dQ < 0 \), with heat released by the system to the bath.

At equilibrium, the terms in the sum of Equ (1) are dominated by clusters of energy shells selected by a sharp peak, arising from the product of a rising number of system states \( \Omega(E) \), and a falling bath factor \( e^{-E/T_{bath}} \). The peak width is the energy fluctuations from stochastic system-bath exchanges. These equilibrium ideas describe states, not processes.

The Partial Equilibration Scenario postulates a plausible post-quench non-equilibrium process for the system to evolve between the initial and the final equilibrium state. A sudden change in bath temperature or quench, will induce a shifted peak, around a different equilibrium state. The post-quench system, initially stranded in non-optimum states, is visualized as moving through the sequentially lower energy shells of Equ (1) in its search for the shifted peak, tracked by an ageing time \( t_w \).

The Scenario postulates that the system i) rapidly spreads ergodically through all states of a shell of energy E, and ii) slowly dribbles out energy \( \delta E \) to the ever-present energy bath. Since the system is partially equilibrated in the quasi-microcanonical shell, the equilibrium definitions can be retained, of the shell entropy \( S(E) \) and its energy derivative \( 1/T_{eff}(t_w) \). The back-and-forth energy exchanges to rapidly surmount internal energy barriers and explore all shell configurations, are summoned by the system from the bath (‘stimulated’). The slow changes on passages to a lower-energy shell, are releases by the system to the bath (‘spontaneous’).

Fig 1 is a schematic of the Partial Equilibration Scenario. The successive shells have lower energy \( E' < E \) and hence lower number of configurations \( \Omega(E') < \Omega(E) \) and entropies \( S(E') < S(E) \). There is a generic entropy barrier \( S_B \equiv -\Delta S = -\ln[\Omega(E')/\Omega(E)] > 0 \) to finding the rarer states. Key seeks lock: most attempts fail.

From an ageing Fluctuation Relation the nonequilibrium energy-change probability is a peak at the origin, times an exponential tail for negative changes. This generic PES signature tail depends on the ageing time through the the effective temperature \( T_{eff}(t_w) \), that scales the heat releases:

\[ P_w(\delta E; t_w) \sim P_0(\delta E; t_w) e^{\delta E/2T_{eff}(t_w)}, \]  

(3)

with an even prefactor \( P_0(\delta E; t_w) \).

In an important result, other effective temperatures, from the Fluctuation-Dissipation Theorem; and from non-equilibrium fluctuations of system variables, are shown to be equal to the PES effective temperature there is only one \( T_{eff} \).

ii) Specific PES from quenching across a transition.

For our case of quenching to T across a first-order transition, the Order Parameter (OP) has to rise from zero, and so the wait times \( t_w \) to reach OP marker events will depend on the quench temperature, \( t_w = t_m(T) \). The effective temperature and PES distribution will thus also depend on the quench temperature, \( T_{eff}(t_w) \) and \( P_0(\delta E; t_w) \rightarrow P_0(\delta E; T) \). The even prefactor \( P_0(\delta E; T) \) can be exponentiated and expanded to quadratic order, Equ (3) is then a gaussian peaked distribution.
avalanches: Four-panel plot of martensite conversion fraction $n_m(t)$ versus time $t$, for fixed $E_0 = 3$, $A_1 = 4$ and different scaled temperatures $|\delta/T| = |T - T_0|/T_0$ as in the legend. There are flat incubations ending in explosive jumps in $n_m(t)$ at $t = t_m$ defined by $n_m(t_m) = 1/2$. (a) tetragonal-orthorhombic transition with Landau spinodal temperature $T_c = 0.9$; (b) cubic-tetragonal transition with $T_c = 0.95$; (c) cubic-orthorhombic transition with $T_c = 0.95$; (d) cubic-trigonal transition with $T_c = 0.97$, that is unusual, see text.

at the origin, times an exponential falloff. Completing the square yields a PES signature of a shifted gaussian, peaked at positive mean changes $M(T) = <\delta E>$, and scaled in $T_{eff}$:

$$P_0(\delta E, T) \simeq e^{-[\delta E - M(T)]^2/2M(T)T_{eff}(T)}.$$  \hspace{0.5cm} (4)

For small heat releases $\delta E = -|\delta E| < 0$, the PES distribution takes a Boltzmann-like form $P_0 \simeq e^{-\frac{1}{2}\beta_{eff}(T)|\delta E|}$. This gives a physical meaning to the effective temperature: it is a search range for accessible energy shells. If $\beta_{eff} \rightarrow 0$, entropy barriers collapse, and passages are immediate. If $T_{eff} \rightarrow 0$, then entropy barriers diverge, and passage-searches freeze.

We postulate that the OP-related bottlenecks can be of two types, depending on the depth of the quench. a) The DW Vapour $\rightarrow$ Liquid delays are attributed to phase space bottlenecks suggested by concepts in protein folding. Hamiltonian energy-spectrum contours in Fourier space of zero energy are like a $T$-dependent Golf Hole (GH) edge, with a negative-energy Funnel region inside it leading to the final state. The entropic delays are from finding and entering the bottleneck.

b) For deeper quenches, the DW Liquid $\rightarrow$ Crystal delays could be conceptually related to spin facilitation models, through the $T$-dependent sparseness of austenitic-hotspot dynamical catalysts, or other facilitating field.

III. DOMAIN-WALL HAMILTONIANS FOR FOUR STRUCTURAL TRANSITIONS IN 3D:

The transition-specific, derived effective Hamiltonians have been presented in detail and we just outline as conceptual background: A) Strains and Compatibility constraints. B) Reduction of continuum strains to discrete-strain ‘pseudo-spins’. C) Reduction of continuum strain free energies to effective ‘spin’ Hamiltonians.

It is useful to define $N_{OP}$ the number of components of the OP strains; and $N_V$ the number of Landau ‘variant’ minima at nonzero OP strain values. In terms of discretized strains, $N_{OP}$ is the number of vector spin components, that can point in $N_V$ variant directions. A double-well Landau free energy for a scalar magnetization maps onto (Appendix A) an Ising model with $N_{OP} = 1$ and $N_V = 2$. We consider four first-order transitions with $N_{OP} = 1, 2, 3, 4$. The nonzero, unit-magnitude variant vectors point respectively to corners of symmetry-dictated polyhedra with $N_V = 2, 3, 6, 4$ corners, inscribed in a unit circle or unit sphere: a geometrically pleasing sequence of line, triangle, hexagon, and tetrahedron. These transitions are respectively, tetragonal-orthorhombic, cubic-tetragonal, cubic-orthorhombic, and cubic-trigonal.
A. Strains and Compatibility:

Strains are symmetric tensors $\mathbf{e} = \mathbf{e}^T$, where the superscript $T$ is Transpose. In three spatial dimensions, there are 6 independent Cartesian strain components $e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{xz}, e_{yz}$. The physical strains $e_1, e_2, \ldots, e_6$ are convenient linear combinations: one compressional $e_1 = \frac{(e_{xx} + e_{yy} + e_{zz})}{\sqrt{6}}$; two deviatoric or rectangular $e_2 = \frac{(e_{xx} - e_{yy})}{\sqrt{2}}$, $e_3 = \frac{(2e_{zz} - e_{xx} - e_{yy})}{\sqrt{6}}$, and three shears $e_4 = e_{xz}, e_5 = e_{yx}, e_6 = e_{xy}$.

The free energy has a nonlinear Landau term that depends on a subset $N_{OP}$ of these physical strains, as the Order Parameter(s). The remaining $n = 6 - N_{OP}$ non-OP Parameter physical strains enter the free energy as harmonic springs, whose extensions cannot be simply be set equal to zero, as pointed out by Kartha. This is because a local OP-strained unit cell will generate non-OP strains in surrounding unit cells. To maintain lattice integrity all strained unit cells must mutually adapt, to OP strains in surrounding unit cells. To maintain lattice

The Compatibility kernels are smallest (eg zero) for specific directions $\hat{k}$, explaining the observed DW orientation along preferred crystallographic directions. The Compatibility potential in coordinate space is an anisotropic powerlaw, with the spatial dimensionality $d = 3$ as the fall-off exponent $\sim 1/R^d$.

B. Discrete-strain pseudo-spins:

The Landau free energy functionals $f_L(\bar{e})$ for a first order transition can be scaled to be independent or weakly dependent, on material parameters. With $N_{OP}$ physical strains as a vector $\mathbf{e}$ in OP space, the Landau free energy $f_L(\mathbf{e})$ in the austenite phase always has a turning point at $\mathbf{e} = \mathbf{0}$. In the martensite phase, it additionally develops $N_V$ variant minima at $\mathbf{e} \neq \mathbf{0}$.

For first-order transitions, the scaled temperature 

and are hence attributed to entropy barriers.

![FIG. 5. Conversion-success fraction: The successfully converting fraction $\Phi_m(T)$ over 100 runs versus $\delta_0(T) \equiv (T - T_c) / T_a$ is shown in the range $T_1 < T < T_0$. The colours of symbols top to bottom denote transitions in order a) tetragonal-orthorhombic, b) cubic-tetragonal, c) cubic-orthorhombic, and d) cubic-trigonal. For a ‘precursor’ region $T_0 > T > T_a$, conversions do not occur. Success fractions are not exponentially sensitive to Hamiltonian energy scales $E_0 = 3, 4, 5, 6$, and are hence attributed to entropy barriers.

$\tau(T) \equiv (T - T_c) / (T_0 - T_c)$.

All energies are scaled in the thermodynamic Landau temperature where austenite and martensite free energies cross, so the scaled $T_0 = 1$. Here $T_a < T_c$ is the spinodal temperature where the austenite minimum vanishes, so uniform bulk austenite becomes unstable for $T < T_c$.

The local vector OP can be written as a product of magnitude and direction $\bar{e}(\bar{r}) = |\bar{e}(\bar{r})| \bar{S}(\bar{r})$. The $N_V$ directions of variant or ‘spin’ vectors $\bar{S}(\bar{r})$ identify the degenerate variants on either side of a Domain Wall (DW), with all having unit magnitude, $\bar{S}(\bar{r})^2 = \sum_{\ell} S_{\ell}(\bar{r})^2 = 1$. Since austenite is always a Landau turning point, and in any case austenite could be induced at any $T$ by local stresses, we always also include the austenite origin point $\bar{S}(\bar{r}) = \mathbf{0}$ as an allowed value.

The strain magnitudes are flat, deep into domains on either side of narrow Domain Walls that are zeros of the OP. The local strain magnitude is set equal to the uniform Landau mean value $|\bar{e}(\bar{r})| \simeq \bar{e}(T) > 0$, so components $\ell = 1, 2, \ldots, N_V$ are approximated as
The Landau free energy density is 

\[ e_{\text{L}}(\vec{r}) \rightarrow \bar{\varepsilon}(T)S_{e}(\vec{r}). \]  

Substituting into the variational free energy density \(^{21}\) with Landau, Ginzburg, and Compatibility terms 

\[ f = f_{\text{L}}(\vec{e}) + f_{\text{G}}(\nabla \vec{e}) + f_{\text{C}}(\vec{e}), \]

generates a \( T \)-dependent effective spin Hamiltonian \( H(\vec{S}, T) \), with the same three terms, inheriting material-specific parameters such as \( T_{\alpha}, T_{0}, A_{1} \). Each of the discretized-strain clock-like Hamiltonians have been systematically derived \(^{21}\) from continuous-strain free energies. They are bilinear in the spins, and encode the crystal symmetries, strain nonlinearities, and Compatibility constraints.

The DW Hamiltonian, with \( E_{0} \) an energy scale (in units of \( T_{0} \)), is 

\[ F = E_{0} \sum_{\vec{r}} [f_{\text{L}} + f_{\text{G}} + f_{\text{C}}] \]

\[ \rightarrow H(\vec{S}, T) = H_{\text{L}}(\vec{S}, T) + H_{\text{G}}(\nabla \vec{S}) + H_{\text{C}}(\vec{S}). \]  

Notice \( H \) has an inherent separation of time scales, with the magnitude \( \bar{\varepsilon}(T) \) responding immediately to quenches \( T < T_{0} \) in a single time-step, while the more sluggish DW adjustments of \( \vec{S}(\vec{r}) \) can take hundreds or thousands of MC time-steps.

With \( \vec{S}^{6} = \vec{S}^{4} = \vec{S}^{2} = 0, 1 \), the Landau term is 

\[ \sum_{\vec{r}} f_{\text{L}}(\vec{e}) \rightarrow \sum_{\vec{r}} f_{\text{L}}(\bar{\varepsilon}\vec{S}) = f_{\text{L}}(T) \sum_{\vec{r}} \bar{\varepsilon}(\vec{r})^{2}. \]  

The Landau free energy density is 

\[ f_{\text{L}}(T) \equiv \bar{\varepsilon}(T)^{2}g_{\text{L}}(T) \leq 0, \]  

defining a factor \( g_{\text{L}}(T) \), that vanishes at the Landau transition temperature \( g_{\text{L}}(T_{0}) = 0 \), and is negative below it.

For a uniform variant \( \vec{S}(\vec{r}) = \vec{S}_{0} \) a constant vector, or in Fourier space \( \vec{S}(\hat{k}) \sim \delta_{\vec{k},0} \vec{S}_{0} \), there is a vanishing of the Ginzburg term \( \sim \vec{k}^{2} \), and of the Compatibility kernel \( \sim \nu_{\bar{\varepsilon}} = 1 - \delta_{\vec{k},0} \). The uniform (Landau) free energy then sets a lower bound to the energy, \( H(\vec{S}, T) \geq Nn_{m}(T)f_{\text{L}}(T) < 0 \), where the martensite fraction is 

\[ n_{m}(t) \equiv (1/N) \sum_{\vec{r}} \bar{\varepsilon}(\vec{r}, t)^{2}. \]

so \( n_{m} = 1 \) or 0 for uniform martensite or austenite.

As a 2D illustration \(^{24}^{26}\), the square-rectangle OP is a scalar, so \( N_{OP} = 1 \). There are two variants (rectangles along either \( x \) or \( y \) axes), so \( N_{V} = 2 \). The Landau free energy \( f_{\text{L}} = \varepsilon^{2}[(\tau - 1) + (\varepsilon^{2} - 1)^{2}] \) is a triple well in the OP strains. For \( \tau = 1 \), the three well depths at \( e = 0, \pm 1 \) are degenerate at zero. For \( 0 < \tau < 1 \) the austenite well at \( e = 0 \) is metastable, and goes unstable at \( \tau = 0 \), the \( T = T_{c} \) spinodal temperature. The Hamiltonian is diagonal in \( \vec{k} \) space, \( \beta H = (D_{0}/2) \sum_{\vec{k}} \varepsilon(\vec{k}, T)|S(\vec{k})|^{2} \), where \( D_{0} = (2\varepsilon^{2}E_{0}/T) \). The energy spectrum for long wavelengths is \( \varepsilon(\vec{k}, T) = -|g_{\text{L}}(T)| + \xi_{0}^{2}k^{2} + A_{1}U(\vec{k}) \). The square-rectangle transition kernel depends on direction \( k = \vec{k}/|\vec{k}| \), or the single polar angle \( \phi \), as

\[ k = \vec{k}/|\vec{k}|, \text{ or the single polar angle } \phi, \text{ as} \]
$U(\vec{k}) = \frac{\nu_{\ell}(k_x^2 - k_y^2)^2}{[1 + (8A_1/A_3)k_x^2k_y^2]} = \frac{\nu_{\ell}(\cos 2\phi)^2}{[1 + (2A_1/A_3)(\sin 2\phi)^2]}$ 

(12)

where $A_3/A_1$ is the ratio of a non-OP (shear) elastic constant, and the non-OP compressional $A_1$. The (positive) kernel has a maximum value $U(max) = 1$ at $\phi = \pm \pi/2$, and a minimum value $U(min) = 0$ at $\phi = \pm \pi/4$, driving a preferred DW orientation along both diagonals.

The energy spectrum for $A_1 = 0$ is a parabola pulled down to negative values by the Landau term, $\epsilon \sim [k^2 - |g_{\ell}(T)|]$.

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The energy spectrum for $A_1 = 0$ is a parabola pulled down to negative values by the Landau term, $\epsilon \sim [k^2 - |g_{\ell}(T)|]$. A zero energy contour in $(k_x, k_y)$ space is a circle with a T-dependent radius $\sqrt{|g_{\ell}(T)|}$, that shrinks to a point at $T_0$. For $A_1 \neq 0$, the bottleneck becomes angularly modulated, with a squared-radius $k^2(T, \phi) = |g_{\ell}(T)| - (A_1/2)U(\vec{k})$, interpolating between a $\phi = \pm \pi/4$ outer radius $k^2_{\text{outer}}(T) = |g_{\ell}(T)|$ and a $\phi = \pm \pi/2$ inner radius $k^2_{\text{inner}}(T) = |g_{\ell}(T)| - (A_1/2)$. The inner radius clearly vanishes at some temperature $|g_{\ell}(T_d)| = (A_1/2)$ where $T_d < T_0$. This characteristic temperature, from an interplay between Landau, Ginzburg, and Compatibility terms, is where the entropy barrier diverges.

Planes et al consider a uniform-martensite model with a Landau variational term $f_L(\varepsilon, T)$. Fast or slow behaviour is through first-passage-time jumps crossing an energy barrier, that collapses at $T_c$, or is largest at $T_0$. Our spatially non-uniform martensite model with Ginzburg, Compatibility and Landau variational terms, differs in detail, but is similar in spirit. Fast or slow behaviour is through MC searches crossing an entropy barrier, that collapses at $T_1$ and diverges at $T_d$.

C. DW Hamiltonians for four transitions:

Clock models have discrete spins directed at $N_V$ points on a unit circle, and are denoted by $\mathbb{Z}_{N_V}$, where the Ising model is $\mathbb{Z}_2$. Here we generalize to include $\vec{S} = \vec{\vec{S}}$, and call these ‘clock-zero’ models, denoted by $\mathbb{Z}_{N_V+1}$.

Drawing on Eqn (7), the generic coordinate-space Hamiltonian is

$$\beta \mathcal{H} = \frac{D_0}{2} \sum_{\vec{r}, \vec{r}'} \sum_{\ell, \ell'} \epsilon_{\ell, \ell'}(\vec{k}) S_{\ell}(\vec{r})^2 + \xi_0^{\vec{k}} \vec{\vec{S}}(\vec{r}) \vec{\vec{S}}(\vec{r})^\dagger \vec{\vec{S}}(\vec{r}) \vec{\vec{S}}(\vec{r})^\dagger, \quad (13)$$

where the overall energy scale is $D_0(T) = 2\xi^2(T)E_0/T$. Here $\xi_0^{\vec{k}}$ is the domain-wall thickness parameter, $A_1$ is the elastic constant for the non-OP compressional strain$\textsuperscript{[20]}$. The kernel $U_{\ell\ell'}$ is an $N_{OP} \times N_{OP}$ matrix potential, that carries the spatial dimensionality $d = 3$, and depends on ratios of other non-OP elastic constants to $A_1$. Local meanfield treatments$\textsuperscript{[22]}$ yield even the complex strain textures of some real material$\textsuperscript{[13,24]}$.

The generic $\vec{\vec{k}}$ space Hamiltonian is obtained from $S_{\ell}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} S_{\ell}(\vec{k}) e^{i\vec{k} \cdot \vec{r}}$, and as $\vec{\vec{S}}(\vec{r})$ is real, $\vec{\vec{S}}(\vec{k})^* = \vec{\vec{S}}(-\vec{k})$. The Hamiltonian and energy-spectrum are

$$\beta \mathcal{H} = \frac{D_0}{2} \sum_{\ell, \ell'} \epsilon_{\ell, \ell'}(\vec{k}, T) S_{\ell}(\vec{k}) S_{\ell}(\vec{k})^\dagger; \quad (14)$$

$$\epsilon_{\ell, \ell'}(\vec{k}, T) = \left[|g_{\ell}(T)| + (2\xi_0^{\vec{k}})(2\xi_0^{\vec{k}})|\vec{k}|^2\right] \delta_{\ell, \ell'} + \frac{A_1}{2} U_{\ell\ell'}(\vec{k}).$$

\begin{figure}[h]
\centering
\includegraphics[width=\columnwidth]{fig8.png}
\caption{Angell-type plot as in glasses, for athermal martensites: The delay times $\bar{t}_m(T)$ are replotted versus $T_d/T$, so that Arrhenius activated times would give a straight line. The x-axis data for the four transitions go from a value of unity on the left, to their respective $T_d/T$ on the right. The obvious curvature shows that delays are not activated over energy barriers. They are attributed to entropy barriers.}
\end{figure}

The 3D transitions are given below in the sequence of $N_{OP} = 1, 2, 3, 4$, plus $N_V = 2, 3, 6, 4$ cases respectively.

\begin{enumerate}
\item \textbf{Tetragonal-Orthorhombic case ($N_{OP} = 1, N_V = 2$)}: The scalar OP is the first deviatoric-strain OP $\varepsilon_{22} = (\varepsilon_{yx} - \varepsilon_{xy})/\sqrt{2}$, with $\vec{\vec{k}}$ having 2 + 1 values: at the origin, and pointing to the two endpoints of a unit-circle diameter. The Hamiltonian is like a 3D Spin-1 Blume Capel model$\textsuperscript{[24]}$, but with anisotropic power-law interactions, and with the quadratic term $f_L(T)\vec{\vec{k}}^2$ where $f_L(T) < 0$. The Hamiltonian is a clock-zero $\mathbb{Z}_{2+1}$ model$\textsuperscript{[21]}$. The scalar compatibility kernel $U(\vec{k})$ for the tetragonal-orthorhombic transition is given in Eqn. (A26) of Ref 21.

With $f_L(T) \equiv \vec{\vec{k}}^2(T)g_{\ell}(T) \leq 0$, the Tetragonal-orthorhombic (and also 2D square-rectangle) case has the squared-mean OP and $g_{\ell}(T)$ factor$\textsuperscript{[21]}$

$$\vec{\vec{k}}^2(T) = \frac{2(3/2)|1 + \sqrt{1 - 3\bar{r}/4}|}; \quad g_{\ell}(T) \equiv \frac{1}{(\bar{r} - 1 + (\vec{\vec{k}}^2 - 1)^2)}.$$

\item \textbf{Cubic-tetragonal case ($N_{OP} = 2, N_V = 3$)}: This 3D transition has been considered earlier$\textsuperscript{[22,24]}$. The
OP strains are the two deviatoric strains \( (e_3, e_2) = ((2e_{zz} - e_{xx} - e_{yy})/\sqrt{6}, (e_{xx} - e_{yy})/\sqrt{2}) \). The spin values \( \vec{S} = (S_3, S_2) \) vectors are in a plane in OP space, with \( \vec{S} \) having 3 + 1 values: at the origin and pointing to the three corners of a triangle inscribed in a unit circle. The Hamiltonian is a clock-zero \( Z_{3+1} \) model. The compatibility kernel is a 2 × 2 matrix, \( U_{\ell'\ell}(\vec{k}) \), with \( \ell, \ell' = 2, 3 \), as in Eqn (A23) of Ref 21.

The mean OP and \( g_L(T) \) of the cubic-tetragonal transition are

\[
\bar{\varepsilon}(T) = (3/4)[1 + \sqrt{1 - 8\tau/9)];
\]

\[
g_L(T) = (\tau - 1) + (\bar{\varepsilon} - 1)^2. \tag{16}
\]

c) Cubic-orthorhombic case \( (N_{OP} = 2, N_V = 6) \):
The OP strains are again the two deviatoric strains \( (e_3, e_2) \) as above. The nonzero \( \vec{S} = (S_3, S_2) \) spin vectors are in a plane in OP space, with \( \vec{S} \) having 6 + 1 values: at the origin and pointing to the six corners of a hexagon inscribed in a unit circle. The Hamiltonian is a clock-zero \( Z_{6+1} \) model. The Compatibility kernel is a 2 × 2 matrix, \( U_{\ell'\ell}(\vec{k}) \), again with \( \ell, \ell' = 2, 3 \) and is the same as the cubic-tetragonal case, given in Eqn (A23) of Ref 21.

The squared-mean OP and \( g_L(T) \) for the Cubic-orthorhombic case, are the same as the tetragonal-orthorhombic in Equ (15).

d) Cubic-trigonal case \( (N_{OP} = 3, N_V = 4) \):
The three OP for the cubic-trigonal transition are the three shears \( e_3, e_5, e_6 = e_{xy}, e_{yz}, e_{zx} \), and the variant vector has three vector components, with \( \vec{S} \) having 4 + 1 values: at the origin and pointing to the four corners of a tetrahedron inscribed in a unit sphere. The Compatibility kernel is now a 3 × 3 matrix, \( U_{\ell'\ell}(\vec{k}) \), with \( \ell, \ell' = 4, 5, 6 \), or six components \( U_{44}, U_{55}, U_{66}, U_{45}, U_{54}, U_{64} \) as in Eqn (A20) of Ref 21.

The mean OP and \( g_L(T) \) for the cubic-trigonal case are the same as the cubic-tetragonal case in Equ (16).

IV. MONTE CARLO SIMULATIONS:

Simulations were done on models for four transitions in 3D. The initial state \( t = 0 \) is 2% randomly and dilutely seeded martensite cells, in an austenite sea of \( \vec{S} = 0 \). Evolutions proceed at quench temperatures \( T < T_0 \). Typical parameters are \( T_0 = 1; E_0^2 = 1; T_e = 0.81 \) to 0.97; \( A_1 = 1 \) to 85; \( E_0 = 3, 4, 5, 6 \); \( N = L^3 = 16^3 \); \( N_{runs} = 100 \); and holding times \( t_h = 10^4 \) MC sweeps, each over \( N \) sites.

The Compatibility kernels arise from the non-OP harmonic terms, with \( (6 - N_{OP}) \) elastic constants. For all transitions, we specify the fixed ratio of other non-OP elastic constants, to \( A_1 \). For the tetragonal-orthorhombic transition, with \( N_{OP} = 1 \) and \( S_2 \) as the OP spin, the non-OP elastic constants are the other deviatoric constant \( A_3 \), and the three shear constants \( A_4, A_5, A_6 \), set to be \( A_3 = A_4 = A_5 = A_6 = A_1/2 \). Similarly, for the cubic-tetragonal and cubic-orthorhombic cases with \( N_{OP} = 2 \) and \( (S_3, S_2) \) as the OP spins, the non-OP constants are set to be \( A_1 = A_5 = A_6 = A_1/2 \). Finally, for the cubic-trigonal case with \( N_{OP} = 3 \) and the shears \( (S_3, S_6, S_6) \) as the OP, the constants are set as \( A_2 = A_3 = A_1/2 \).

The standard MC procedure \( 22 \) is followed, with an extra data retention \( 13 \) of energy changes.

0. Take \( N \) lattice sites, each with a vector spin of \( N_{OP} \) components, in one of \( N_V + 1 \) possible values (including zero) at MC time \( t \). Each \( \{\vec{S}(t)\} \) set is a ‘configuration’. With \( n_m = 0 \) or 1 for uniform austenite or martensite, the average martensite fraction is \( n_m(t) \leq 1 \). The conversion time \( t_m \) is defined as when \( n_m(t_m) = 1/2 \).

1. Randomly pick one of \( N \) sites, and randomly flip the spin on it to a new direction/value, and find the (positive or negative) energy change \( \delta E \).

2. If \( \delta E \leq 0 \), then accept the flip. If \( \delta E > 0 \), then accept flip with probability \( e^{-\delta E/T} \). Record this spin-flip \( \delta E \), that is usually not retained after use.

3. Repeat steps 1 and 2. Stop after \( N \) such spin-flips. This is the \( t + 1 \) configuration with \( n_m(t + 1) \).

4. We collect all recorded \( \{\delta E\} \) over each MC sweep of every run while tracking \( n_m(t) \). The collection is only up to a waiting time equal to the martensite conversion time. \( t = t_w \leq t_m(T) \leq t_h \). We do six quenches, from \( T = T_1 \) upwards to \( T_d \).

A single-variant athermal martensite droplet or ‘embryo’ \( 14 \) can form anywhere, and after a local conversion at a waiting time \( t_w = t_m \), can propagate rapidly to the rest of the system \( 11 \). Hence it is the mean rates \( \bar{r}_m \) (or inverse times), that are averaged over \( N_{runs} \) runs, analogous to total resistors in parallel determined by the smallest resistance. The mean times \( \bar{t}_m \) are defined as the inverse mean rates \( 23 \)

\[
\bar{r}_m(T) = \frac{1}{N_{runs}} \sum_{n=1}^{N_{runs}} \frac{1}{t_m(n)}; \bar{t}_m(T) = \frac{1}{\bar{r}_m(T)}. \tag{17}
\]

For an unsuccessful \( n \)-th run that does not convert in a holding time \( t_h \), the rate \( r_m(n) \) could be assigned a value of either \( 1/t_h \) (conversion right after cutoff) or 0 (conversion never occurs). We choose the \( 1/t_h \) cutoff, that shows up as a flattening of the mean rate near \( T_d \). An extrapolation of the linear part of \( r_m(T) \) to the temperature axis yields a value \( 23 \) for \( T_d \).

V. DELAYS AND BOTTLENECKS:

For the four transitions, we consider i) Delays from sluggish Domain Walls; ii) Bottlenecks in Fourier space.

A. Delays from sluggish Domain Walls

Figure 2 shows the twinned microstructures in all four transitions, colour coded through the variant-label \( V \), where \( V = 0 \) is always austenite. For the single-OP
tetragonal-orthorhombic transition, \( V = \pm 1 \) has two variant colours. For the two-component OP, the cubic-tetragonal and cubic-orthorhombic transitions have respectively, \( V = 1, 2, 3 \) and \( V = 1, 2, \ldots, 6 \) variant colours. For the three-component OP, the cubic trignon has \( V = 1, 2, 3, 4 \) four variant colours. Fig 2 shows that all allowed degenerate \( N_V \) variants are present, for all four transitions.

The tetragonal-orthorhombic, and cubic-tetragonal twins can have Domain Walls decorated with austenite, as also found in the 2D case\(^{23}\). Such observed austenite retention\(^{23}\) can be understood: they are energetically favoured, when the lower Ginzburg costs of austenite-martensite walls compensate for the absence of the negative condensation energy \( f_L(T) < 0 \) of martensite unit cells. As \( T \) is lowered, the energy accounting is reversed, and the austenite inclusions are expelled, replaced by martensite, so DW are only between martensite variants\(^{23}\).

We define a fractional deviation from a characteristic temperature \( T_d \), as

\[
\delta_0(T) \equiv (T - T_d)/T_d \leq 0. \quad (18)
\]

Figure 3 shows the martensite conversion-fraction \( n_m(t) \) versus MC time \( t \) in a single run, for different \( \delta_0(T) \). For quenches to below \( T = T_1 \), there is an immediate avalanche conversion in a single \( t = 1 \) sweep, characteristic of athermal martensite. For temperatures \( T > T_1 \) there is a strange ‘incubation’ behaviour, or a postponement of these avalanches. The fraction \( n_m(t) \) remains virtually unchanged, up till \( t = t_m \) when \( n_m(t) \) rises sharply through 1/2, to unity. The cubic-trigonal transition has \( N_{OP} = 3 \) order parameter components, \( N_V = 4 \) variants, and can show unusual behaviour. Here, there is an initial jump to \( n_m = 1/2 \) followed by incubation, and then a jump to unity.

Fig 4 shows that for \( T < T_1 \) there is an immediate spike in the MC acceptance fraction \( A_{acc}(t) \) at \( t = 1 \), and drop in energy \( E(t) \) to negative values. For \( T > T_1 \), during incubations they both remain zero, up to \( t = t_m(T) \), when the acceptance spikes and the energy drops. Again, the cubic-trigonal case is unusual.

What goes on microscopically, during incubation ? In 2D, Video\(^{23}\) shows random initial seeds of both variants (red,blue) can quickly form an almost zero energy single-variant martensitic droplet or embryo (red) in an austenite background (green), in the DW Vapour state. The small droplet extends and retracts amoeba-like arms, searching for energy-lowering pathways. After a long conversion delay \( t_m \) of hundreds of time steps, when \( n_m \approx 0 \), the single-variant droplet (red) suddenly expands rapidly and generates the opposite variant (blue). This is the wandering-wall or DW Liquid state. After a shorter orientation delay, the walls of the DW Liquid orient to a DW crystal.

Figure 5 shows for all four transitions, the mean fraction of successful conversions \( \Phi_m \) during a holding time
t = t_h over 100 runs, versus the temperature deviation \( \delta_0(T) \). For temperatures \( \delta_0 \leq -0.1 \), every run converts, and \( \Phi_m = 1 \). However, for \( \delta_0 > -0.1 \), \( \Phi_m(T) \) falls through 1/2 at \( \delta_0(T) \sim -0.05 \), and then to zero. The success fraction is not exponentially sensitive to overall energy scales \( E_0 = 3, 4, 5, 6 \), so the probability of conversion is not activated over an energy barrier.

Just above \( T_2 \) there are unsuccessful runs (not shown), when the martensite seeds can dissolve back into austenite. The seeds will not be regenerated, even if the holding time \( t_h \) is increased, or if the temperature is lowered.\(^{20}\)

Figure 6 shows a linear-linear plot of the mean conversion times \( \bar{t}_m \) versus \( \delta_0(T) \) for various \( E_0 \). The absence of exponential sensitivity to \( E_0 \) implies the delays are not activated over energy barriers, but are due to entropy barriers. For \( T < T_1 \) fluctuations are small, while for \( T > T_1 \) standard-deviation error bars \( \pm \sigma \) over the \( N_{\text{run}} = 100 \) runs, are larger, on approaching \( T_d \).

If the probability of entropy-barrier crossings coming from a product of sequential random steps, a logarithm of rates would be an additive random variable, suggesting a log-normal distribution of rates\(^{23}\) \( P(r_m) \). Fig 7 shows optimized-bin histograms\(^{27}\) of \( r_m \) data, with (asymmetric) log-normal lines as guides to the eye. Although data are too sparse to decide distributions, clearly fast conversions are narrow, and slow conversions are broad, similar to protein folding.\(^{28,29}\)

Fig 8 shows an Angell-type plot\(^{29}\) of log delay time versus \( T_d/T > 1 \). Arrhenius-type activations over energy barriers would be linear. The delays have curvatures, and so must be from entropy barriers. The solid curve is VFT behaviour of Equ (29) below, with \( B_0 = 0.25 \).

B. Bottlenecks in Fourier-space:

We draw on concepts of protein folding\(^{25,30}\), to understand the entropy barrier delays.

A purely random search of protein configurations could take astronomical times (Leventhal paradox). Rapid protein folding is attributed to a configuration-space Golf Hole (GH) opening into a Funnel of negative-energy \( E \) states,\(^{28,29}\) Bicout and Szabo\(^{30}\) consider a random walk of a Brownian particle in a space of eigen-labels of protein folding modes (that could be analogous to propagative martensitic twinning modes\(^{35}\)). The Brownian particle has to locate and enter spherical zero-energy GH contour of marginal modes. Unusual delays can occur, at the GH edge.

In our case, the bottleneck is fixed by the energy spectrum from Equ (14) in 3D Fourier space (taken as diagonal in \( \ell \), for discussion):

\[
\epsilon_{\ell\ell}(\vec{k}, T) = \xi_0^2 |\vec{k}|^2 - |g_L(\tau)| + (A_1/2)U_{\ell\ell}(\vec{k}).
\]

Energy spectra set to a constant \( C \) or \( \epsilon_{\ell\ell}(\vec{k}, T) = C \), define contours in \( \vec{k} \)-space. The Ginzburg term at long wavelengths \( \sim |\vec{k}|^2 \), forms a \( \vec{k} \)-space spherical bowl in 3D, with zero-energy minimum at the origin. The Compatibility term \( U_{\ell\ell}(\vec{k}) \) angularly modulates its 2D surface to produce an anisotropic zero-energy contour\(^{22}\).

The phase-space boundary \( \epsilon_{\ell\ell}(\vec{k}, T) = 0 \) separates an outside \( \vec{k} \) region of positive (austenite) energies, from a \( \vec{k} \)-region inside, of (martensitic) negative energies. Video B shows\(^{22}\) a 2D circular droplet Fourier profile in \((k_x, k_y)\) as it distorts, to enter the phase space bottleneck.

We consider spectra with \( \epsilon_{22}(\vec{k}, T) \) for the first three transitions, and \( \epsilon_{66}(\vec{k}, T) \) for the cubic-trigonal case.
FIG. 13. Variance of the even-symmetry prefactor : Four-panel linear-linear plot of the variance $\sigma^2(T)$, of the prefactor $P_0^{\pm}(\delta E, T)$, versus $T_{eff}(T)/M(T)$ for the four transitions. The energy scale is chosen as the (positive) mean energy change $M(T) \equiv \delta E$ over the entire PES distribution.

Consistent with the twin orientations in Fig 1, the plane intersecting the 3D bottleneck to yield a 2D cross-section is taken as $[\hat{k}_x, \hat{k}_y, \hat{k}_z] = [1, 1, 1]$. The plane through the Brillouin Zone origin is $\hat{k}_x + \hat{k}_y + \hat{k}_z = 0$, and Fig 9 shows for all four transitions, the $T$-dependent contours of constant $\epsilon_{\ell \ell}(k_x, k_y, k_z = -k_x - k_y, T) \text{versus } (k_x, k_y)$ for temperature range $\delta_0(T) = -0.1$ to +0.2. As mentioned, the cubic-tetragonal and cubic-orthorhombic have the same kernel but different Landau factor $g_L(T)$, so one would expect the second and third panels to show the same overall shapes, but slightly different energy contours for a given $T$: this is indeed the case.

The bottleneck sizes are large at low $T$ and small at high $T$. The contours are angularly modulated between the Landau temperature, $k^2_{outer}(T) = |g_L(T)| = 0$. Close to transition,

$$k^2_{outer}(T) \simeq b(T_0)(T - T_0)$$

where the Taylor expansion coefficient $b(T) \equiv -d g_L(T)/dT < 0$.

With a positive $U_{\ell \ell}(max) > 0$ there is a temperature $T_d < T_0$ where the inner radius can pinch off to zero, $k^2_{inner}(T_d) = |g_L(T_d)| - (A_1/2)U_{\ell \ell}(max) > 0$, while the outer radius is still nonzero. Near $T_d$,

$$k^2_{inner}(T) = |g_L(T)| - |g_L(T_d)| \simeq b(T_d)(T - T_d).$$

Figure 10 shows the inner and outer squared-radius, both almost linear, and vanishing respectively at $T_d$ and $T_0$.

The conversion-delay divergence comes from a pinch-off of the inner radius $k^2_{inner}(T)$ of the bottleneck. The topology of a 2D slice of the 3D negative energy states, goes from an open butterfly to a segmented four-petalled flower.[22] It is impossible for the broad Fourier profile of a small droplet to distort at zero total energy, into four separated petal-like segments. The lower-energy states for $T > T_d$ are thus available, but not accessible. The inter-shell configurational pathway closes; the success-fraction vanishes; and the entropy barrier diverges.

VI. PES SIGNS IN ALL FOUR TRANSITIONS

We now exhibit PES signatures in the four athermal martensite transitions. Entropy barriers are insensitive to energy scales, so we consider only $E_0 = 3$.

FIG. 14. Normalized probabilities $P_0$ of energy-changes in linear-linear plot: Four-panel Figure for all transitions, showing the probability $P_0(\delta E, T$) versus energy change $\delta E$ for the six quench temperatures $T$ in the legend. The probabilities are consistent with the predicted PES signature of shifted Gaussians peaked near a mean energy changes $M(T) > 0$, with exponential heat-loss tails for $\delta E < 0$.

As noted the MC procedures of Section IV retain the set of single spin-flip energy changes $\{\delta E\}$ from all $N$ spin-flips, in each of $N_{run}$ runs, up to $t$ MC times $t \leq t_m(T)$. The histograms can be dense since the data set size can be large: $N \times t_m \times N_{run}$ has up to $10^3 \times 10^4 \times 100$ data points.

An ageing-state fluctuation relation is postulated.[3] The probability $P_0(\delta E, T$) to hit configurations $E'$ from
Solution is entropy change is odd, \( \Delta S \). The ratio of forward and backward probabilities \( R_0(\delta E) \) is related to the entropy change and entropy barrier \( \Delta S(\delta E) = S(E') - S(E) \equiv -S_B < 0 \). Thus

\[
R_0 \equiv \frac{P_0(\delta E, T)}{P_0(-\delta E, T)} = \frac{\Omega(E')}{\Omega(E)} = e^{\Delta S(\delta E)}. \tag{23}
\]

Fig 11 shows four-panel log-linear plots of the fluctuation ratio \( R_0(\delta E, T) \). Since \( R_0(\delta E)R_0(-\delta E) \equiv 1 \), the entropy change is odd, \( \Delta S(\delta E) + \Delta S(-\delta E) = 0 \), and a solution is

\[
P_0(\delta E, T) = P_0^{(+)}(\delta E, T) e^{\frac{1}{2} \Delta S(\delta E)}, \tag{24}
\]

where the (even) prefactor is the geometric mean, \( P_0^{(+)}(\delta E, T) = \sqrt{P_0(\delta E, T)P_0(-\delta E, T)} \). For small energy changes, \( S(E + \delta E) - S(E) \approx \beta_{eff}\delta E \), and hence \( P_0(\delta E, T) \approx P_0^{(+)}(0, T) e^{\frac{1}{2} \beta_{eff}(T)\delta E} \).

Fig 12 is just a check that the prefactor \( P_0^{(+)}(\delta E, T) \) versus \( \delta E \) has no linear contribution near the origin, that might modify the exponential tail. For temperatures near \( T_1 \) it is a single-peak gaussian, while near \( T_d \) it can go bimodal.

Fig 13 shows that the variance \( \sigma^2 \) of the weight \( P_0^{(+)}(\delta E, T) \) versus a scaled \( T_{eff}(T) \) is linear and nonsingular, for all four transitions.

Fig 14 shows four-panel linear-linear plots of (normalized) \( P_0(\delta E, T) \) versus \( \delta E \) for four transitions, each at one of six temperatures in the Legend. The peak is at positive energy as in the oscillator case and moves left as \( T \) decreases towards \( T_1 \). The exponential tails near the origin are barely visible.

Fig 15 shows the same four plots but now in log-linear form, and zoomed in. The curves all show the PES signature of linearity around the origin \( \delta E = 0 \). The cubic tetragonal panel has been shown earlier. As \( T \) is lowered to \( T_1 \), the slopes \( \beta_{eff}(T)/2 \) all flatten.

Fig 16 shows a central result, namely the search temperature \( T_{eff}(T) \) and its inverse, \( \beta_{eff}(T) \) versus \( T \). The left-axis search temperature \( T_{eff}(T) \) intersects the temperature axis at an extrapolated \( T_{eff}(T_d) = 0 \), defining a quench temperature \( T_d \). The vanishing appears to be linear, \( T_{eff}(T) \sim T - T_1 \) at a search explosion temperature \( T_1 \).

The mean conversion rate involves an integral over the heat releases of the distribution.\(^{[50]}\) The mean time is then a singular exponential \( t_m \approx t_0 e^{M/T_{eff}} \approx t_0 e^{\beta_{eff}(T_d)/(T-T_1)} \). The Vogel Fulcher-Tammann formula thus emerges naturally from a search temperature freezing inducing a rapid arrest of PES cooling, and an entropy-barrier divergence.

Similarly, the inverse effective temperature \( \beta_{eff}(T) \) on the right-axis of Fig 16 seems to go to zero linearly \( (T - T_1) \) at a search explosion \( T_1 \) where entropy barriers vanish.

Once again, the cubic-trigonal last panel is unusual, with \( T_{eff} \) showing a smaller slope near \( T_d \). If the linear slope actually vanishes as \( T_{eff}(T) \sim (T - T_d)^2 \) then that would yield ‘super-VFT’ behaviour of \( t_m \sim e^{1/(T - T_d)^2} \).
Fig. 17 shows the scaled ratio of occurrence probability to its value at the origin, \( \Pi_0 \equiv P_0(\delta E,T)/P_0(0,T) \) versus \( z \equiv \beta_{\text{eff}}\delta E/2 \). The four dashed white lines have slopes close to the predicted universal slope of unity, as given in the Figure caption.

The normalized probability \( P_{MC} \) of a Monte Carlo spin-flip is the product of the occurrence probability \( P_0 \) and an MC acceptance factor with step functions,

\[
P_{MC}(\delta E,T) = \frac{P_0(\delta E,T)}{N_{MC}(T)} \left[ \theta(-\delta E) + e^{-\delta E/T} \theta(\delta E) \right],
\]

with \( N_{MC}(T) \) a normalization constant. The ratio of the MC probability and its value at the origin defines \( \Pi_{MC}(\delta E,T) \equiv [P_{MC}(\delta E,T)/P_{MC}(0,T)] \). With \( z \equiv \beta_{\text{eff}}(T)\delta E/2 \),

\[
\Pi_{MC} \approx [e^{z\theta(-\delta E)} + e^{-z[(2T_{eff}/T)-1]\theta(\delta E)}]/N_{MC}(T).
\]

Fig 18 shows a log-linear plot of \( \Pi_{MC} \) along the positive axis \( z = \beta_{eff}\delta E/2 > 0 \). The closeness of data to theoretical lines with slope \( [1 - 2T_{eff}/T] \) is further evidence for PES.

In conclusion all four transitions show PES signatures, lending support to the Partial Equilibration Scenario.

VII. PES DELAYS IN SIMULATIONS AND EXPERIMENT

We show that delay data both in simulations and in experiment, are consistent with a picture of diverging entropy barriers from linearly vanishing PES effective temperatures.

A. VFT delays in 3D simulations

Vogel-Fulcher-like behaviour in simulations: Four-panel plot of scaled data in simulations of log-linear scaled \( \beta_0(t_0) \) versus scaled \( B_0/|\delta_0(T)| \), for the four transitions a),b),c), d), with each panel showing \( E_0 = 3,4,5,6 \). Data clustering for small \( |\delta_0(T)| \), on the dashed line over three orders of magnitude is evidence for Vogel-Fulcher behaviour. For lower temperatures, there is a peel-off towards the x-axis near \( T = T_1 \) (downward arrow).
be written near $T_d$ as

$$\bar{t}_m(T) = t_0 e^{B_0 T_d / |T - T_d|} = t_0 e^{B_0 / |\delta_0(T)|}$$

(27)

where $t_0, B_0 T_d$ are the time and energy scales, for DW shifts of a lattice spacing.

The logarithms of VFT times can be written in two useful forms, to extract constants $B_0, t_0$ from simulations and experiments. Thus

$$\frac{1}{\ln t_m(T)} = \frac{(|\delta_0(T)| / B_0)}{[1 + (\log t_0)(|\delta_0(T)| / B_0)]}$$

(28)

and

$$\ln t_m(T) = \log t_0 + [B_0 / |\delta_0(T_0)|].$$

(29)

For simulations, $B_0$ and $t_0$ can be extracted from data using Equ (28) and Equ (29). Fig 19 shows for all four transitions, the data in a scaled form of

$$\ln(t_m / t_0) = B_0 / |\delta_0(T)|.$$  

(30)

There is data clustering around the Vogel-Fulcher straight line showing universality over 3 orders of magnitude near $T_d$. There is also a peel-off toward shorter times, near $T_1$ (downward arrow).

B. VFT delays in martensitic alloys

Delayed athermal martensite transformations in metallic alloys have been tracked by conversion diagnostics suited to the scale of the waiting times such as electrical resistivity drops; or surface optical or X-ray reflectivity. In pioneering experiments, Kakeshita et al used resistivity drops to detect the austenite to martensite delayed conversions for alloys $Fe_xNi_{1-x}$. The alloying percentage 100 $z$ is 29.9, 31.6, 32.1%, with start temperatures of $M_s = 239, 177, 148$ K. The delays discovered were of macroscopically long times. Other work such as the Klemradt group on NiAl alloys, also rose rapidly: for temperature increments above the $M_s$ values of 0.1 K, 0.6 K and 0.7 K, the delay times went from several seconds, to $10^4$ seconds, to forever.

The data analysis of simulations is used again for experiment, as now described in more detail. To extract divergence temperatures $T_d$ from simulation or experimental data, we plot $1 / \ln(t)$ versus $T$, and extrapolate straight line segments to the x-axis (not shown). For FeNi data $T_d$ this yields $T_d \approx 247, 187, 158$ K, well above $M_s$, with large fractional delay windows $|\delta_0(M_s)| = |T_d - M_s| / T_d = 0.03, 0.05, 0.66$. Similarly extrapolation of data for the NiAl alloy with $M_s = 282.2$K yields $T_d = 283K$ but with a smaller window $|\delta_0(M_s)| \approx 3 \times 10^{-3}$.

Another group considered NiTi alloys, and argued that if the largest delay is at $T = T_0$, then for a long enough annealing time, conversions should be seen at any $T$ in a wide window $M_s < T < T_0$. However no conversion was detected, for holding at $T = 275.9$ above $M_s = 274.3K$, for $t_0 = 21$ days. The absence of conversion was attributed to a sparseness of (atomic) catalyst fields in facilitation-type delay models. In our picture this absence could also be due to $T$ being outside the narrower conversion window $M_s < T < T_d < T_0$.

Fig 20 shows measurement data of conversion times $t$, in seconds, versus temperature $T$ in degrees Kelvin. The left column shows a linear-linear plot like Equ (28) of $1 / \ln(t)$ versus $|\delta_0(T)|$ to extract slope $1/B_0$ from Kakeshita data for three alloys of FeNi (top panel); and from Klemradt data for a NiAl alloy (bottom panel). The right column shows a linear-linear plot Equ (29) of $1 / |\delta_0(T)|$, using lines of the extracted slope $B_0$, to determine the intercept $t_0$ for FeNi (top panel) and for NiAl (bottom panel). Downward arrow marks $T_1$ for NiAl data. The 'fragility' parameter $B_0 T_d = 1.23K$, and a basic time scale for DW hops is $t_0 = 1$ second.

FIG. 20. Vogel-Fulcher-like behaviour in experiment: Left column shows data from both groups in a $1 / \ln(t)$ versus $|\delta_0(T)|$ plot. The slope $1/B_0$ is extracted from a fit to $y = (1/B_0)x$. Right column again shows results of both groups, in a log-linear plot of $\ln t_m$ versus $1/|\delta_0(T)|$. The NiAl data show a downward deviation towards $T = M_s$ marked by the downward arrow. Using the extracted $B_0$ values, the intercepts are found in a fit to $y = B_0 x + y_0$.

Fig 21 shows that combined experimental data, cluster around the Vogel-Fulcher straight line of Equ (30), with universality over 3 orders of magnitude near $T_d$. For NiAl data, there is a linear falloff on approaching $T_1$ (downward arrow), consistent with Fig 16.

It would be interesting to get more data for these and other martensitic alloys, through systematic quenches in steps of $1/|\delta_0(T)|$, over the entire delay range $M_s < T < T_d$ between barrier divergence and collapse. It would also be interesting to include a $T_1$-like onset of sluggishness, in fitting analyses of glass-former viscosity data.
VIII. SUMMARY AND FURTHER WORK

In this paper, we present Monte Carlo (MC) simulations, on discrete-strain Hamiltonians for four 3D structural transitions, under systematic temperature quenches from seeded austenite, to study austenite-to-martensite conversion times. The results and scenario are as follows.

For athermal martensites, there are explosive conversions below a martensite start temperature \( M_s \) so there are no barriers. Above this start temperature, entropy barriers emerge, and incubation time delays rise sharply towards a divergence temperature \( T_d \). The entropy barrier collapse/divergence, is understood through temperature-controlled phase-space bottlenecks.

Partial equilibration ideas provide an understanding of fast/slow times, based on effective temperatures for energy-lowering searches. The inverse search temperature vanishes linearly at \( M_s \) or \( 1/T_{eff}(T) \sim |T-M_s| \to 0 \). The search temperature vanishes linearly at \( T_d \), or \( T_{eff}(T) \sim |T-T_d| \to 0 \). This rapid search arrest explains the singular Vogel-Fulcher-Tammann form, extracted from martensitic experimental data.

Further simulations of crystallisation models could try to record heat releases. Further experiments could record strain signals and intermittency over the delay region \( T_d > T > T_1 \); and over the tweed precursor region above it \( T_0 > T > T_d \). Non-stationary distributions of energy changes in martensites could be measured through concurrent acoustic, photonic or strain probes. The VFT temperature regime in glasses shows non-Debye frequency responses, this might be more general. Finally, quenches of complex oxides near their structural/functional transitions, might yield interesting PES signatures in functional variables, induced by their coupling to ageing strain domains.

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Appendix A: PES signatures in the \( m^4 \) model:

As a toy model illustration of the Section III procedure we consider a 2D magnetization free energy with double-well Landau term and a Ginzburg term, \( F = E_0 \sum_r [f_L + f_G] \). Here \( m \) is the single component OP, of both signs, so \( N_{DP} = 1, N_V = 2 \). The Landau term is

\[
f_L(m(\vec{r})) = \epsilon(T) m(\vec{r})^2 + m(\vec{r})^4/2 \tag{31}\]

where \( \epsilon(T) \equiv (T - T_c)/T_c \), with all energies/temperatures scaled in the physical transition temperature, so the scaled \( T_c = 1 \). The Ginzburg term is \( f_G = \xi_0^2 (\Delta m(\vec{r}))^2 \).

Domain-walls are solitonic solutions with a tanh profile, interpolating between flat OP variants of opposite sign, within a DW thickness \( \xi_0 \sim 1 \). The OP can be written as a magnitude \(|m|\) times a variant ‘spin’ \( S(\vec{r}) = \pm 1 \) of unit length. The nearly flat magnitude in the domains is approximated by the mean field OP,

\[
m(\vec{r}) \equiv |m(\vec{r})|s(\vec{r}) \to \bar{m}(T)S(\vec{r}) \tag{32}\]

where \( \bar{m}(T) \equiv |\epsilon(T)|^{1/2} \). Compare Equ (7).

The mean-field Landau free energy is

\[
f_L(T) = \bar{m}(T)^2 g_L(T); \quad g_L = -\frac{1}{2}|\epsilon(T)| < 0. \tag{33}\]

where \( g_L(T_c) = 0 \). Compare Equ (10).
Substituting Equ (32) in Equ (31) yields the DW coordinate space Hamiltonian, with $D_0 \equiv 2\bar{m}^2E_0/T$

$$\beta H = (D_0/2) \sum_r [-|g_L(T)|S(\vec{r})^2 + \xi_0^2(\Delta S(\vec{r}))^2], \quad (34)$$

although in this case, $S(\vec{r})^2 = 1$ at all sites. With $S(\vec{r}) = \sum_\vec{r} e^{i\vec{k}.\vec{r}}S(\vec{k})/\sqrt{N}$, the Hamiltonian in Fourier space is

$$\beta H = (D_0/2) \sum_\vec{k} [-|g_L(T)| + \xi_0^2\bar{K}(\vec{k})^2]S(\vec{k})^2. \quad (35)$$

Compare Equ (13) and Equ (14).

We can do MC simulations with this T-dependent, Ising-variant effective Hamiltonian. The parameters are $N = 64^2, \xi_0^2 = 1, N_{\text{run}} = 10$, with holding times $t_h = 10^5$. The spin-flips are $S = \pm 1 \rightarrow \mp 1$. Fig 22a shows the magnetization fraction $n_m(t)$ versus waiting time $t_w$ analogous to Fig 3, but here with a gradual rise, and no incubation behaviour.

We record $\{|\delta E\}$ for every spin flip up to an OP marker event time $t_w = t_w(n_m(t_m) = 1/2)$. For nearest-neighbour couplings on a square lattice, the energy changes $\delta E$ will be discrete. Fig 22b shows the log-linear $P_0(\delta E, t_w = t_m)$ versus discrete energy changes $\delta E$. The spike heights decrease linearly with energy changes, consistent with PES. Compare Fig 15.

$$\delta E \sim \sum_{\vec{r}} e^{i\vec{k}.\vec{r}}S(\vec{k})/\sqrt{N}. \quad (36)$$

The energy vanishing $E(T)/D_0 \simeq -|g_L(T)| + \{|\xi_0^2[K(\vec{k})] + (A_1/2)[U_{\ell,\ell}(\vec{k})]\}$. \quad (37)

We define ‘athermal’ behaviour as a nonzero $T_1$; explosive conversions for $T < T_1$; and incubation delays in the window $T_1 < T < T_d < T_0$. The behaviour not precisely athermal, is called ‘mixed’, with conversions occurring gradually, without flat incubations. Vanishing of the athermal case start temperature $T_1(A_1, T_c) = 0$ then determines a phase boundary.

The four-panel Fig 24 plot of $T_c$ versus $A_1$ solid line the theoretical boundary between athermal and mixed materials. Simulation data for athermal (open circles) and mixed (open squares) behaviour, are consistent with the theoretical curve.

Fourier space. With $|\bar{S}(\vec{k})|^2$ approximated by a constant, the Hamiltonian energy of Equ (18) is $E/D_0 \sim \sum_{\vec{k}} \epsilon(\vec{k})$ then involves averages of terms over the Brillouin Zone, denoted by square brackets. The droplet energy is

$$E(T)/D_0 \simeq -|g_L(T)| + \{|\xi_0^2[K(\vec{k})] + (A_1/2)[U_{\ell,\ell}(\vec{k})]\}.$$

The four-panel Fig 24 plot of $T_c$ versus $A_1$, shows the phase boundary. Above the phase boundary the system is purely athermal, while below the phase boundary where $T_1 = 0$, is a mixed regime. Data from Fig 23 and other TTT diagrams are seen to be consistent with the theoretical phase boundary. Fig 23 shows that for some parameters, curves on the upper left, have a fall and then a rise with temperature, like a ‘U shape, or downward ‘nose’. For the large $E_0 = 3$ used, the shape is distorted, but for smaller $E_0 < 1$ the U shape is more well defined. The shape is from an Arrhenius activation over a temperature-dependent energy barrier.
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Video D. The $\vec{r}$-space tweed precursor: This shows dynamical tweed in the region $T_0 > T > T_d$, as an array of vibrating martensitic islands in an austenite sea, possibly induced by a $\vec{k}$ space profile, vibrating on top of a topologically blocked bottleneck.

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The mean equilibration rate is the average over an inter-shell rate $1/t(\delta E)$ over all heat releases. With a normalized PES probability, $1/\bar{t} = \int_{-\infty}^{0} d\delta E P_0(\delta E,T)/t(\delta E)$. For slow inter-shell variation $1/t(\delta E) \simeq 1/t_0$, the mean rate is proportional to the acceptance fraction over energy decrements. Taking the PES probability, as a shifted gaussian with peak mean energy change $M > 0$, and variance $\sigma^2 = 2M\tau_{eff}$, the acceptance fraction is a complementary error function, whose asymptotic behaviour yields $t_0/\bar{t} \simeq e^{-M/4\tau_{eff}}$. Dropping constants, the martensitic mean conversion time near $T_d$ is written simply as $\tau_m(T) = t_0 e^{1/2\tau_{eff}(T)}$.

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Activated times $t = e^{U(T)/T}$ over rising energy barriers $U(T) = a + bT^2$ diverge at $T = 0$. The times fall for $T$ increasing from zero, have a minimum, and then rise exponentially at large $T$. The minimum in $U(T)/T$ is at $T^* = \sqrt{a/b}$. Close to $T^*$, the TTT curve has an ‘isothermal’ U-shape or nose: $t(T)/t(T^*) = e^{2(ab)^{1/2}/(T/T^*-1)^2}$. 

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