Understanding glass-like Vogel-Fulcher equilibration times: microcanonical effective temperatures in quenched 3D martensites

N. Shankaraiah\textsuperscript{1}, K.P.N. Murthy\textsuperscript{2} and S.R. Shenoy\textsuperscript{1}

\textsuperscript{1}Tata Institute of Fundamental Research-Hyderabad, Hyderabad, Telangana 500046, India.
\textsuperscript{2}Dept of Physics, Central University of Rajasthan, Bandar Sindri, Rajasthan 305817, India.

(Dated: December 7, 2021)

We do Monte Carlo simulations of four 3D structural transitions through vector-spin models of martensitic strain domains, to test a generic post-quench Partial Equilibration Scenario (PES) of Ritort. We indeed find that the PES distribution from locating downward passages between fixed-energy shells, has an exponential tail in heat releases scaled in an effective search temperature. A linear vanishing of this \( T_{\text{eff}} (T) \sim T_d - T \) at a temperature \( T_d \) where passage-searches freeze, explains the Vogel-Fulcher divergence of equilibration times extracted from martensitic alloy data.

How do systems re-equilibrate after a quench? For thermal quenches to a low temperature \( T \), activated jumps over energy barriers \( \Delta U \) are relatively rarer. Sets of competing rates are dominated by entropy barriers \( S_B > 0 \) to finding re-equilibration pathways at almost constant energy, \( \{ e^{-(\Delta U - T \Delta S)/T} \} \rightarrow \{ e^{\Delta S} \equiv e^{-S_B} \} \).

Ritort and coworkers\textsuperscript{11,12} have proposed a Partial Equilibration Scenario (PES) for re-equilibrations dominated by entropy barriers. Over a waiting time \( t_w \), a post-quench aging system rapidly explores configurations of energy \( E(t_w) \), entropy \( S(E) \), and (inverse) microcanonical effective temperature \( 1/T_{\text{eff}} (t_w) = dS(E)/dE \). Passages to a lower shell of \( E(t_w+1) \equiv E' = E(t_w) + \delta E \) are driven by intermittent spontaneous energy releases \( \delta E < 0 \) to the heat bath at \( T \). The PES says that an iteration of these aging steps ratchets the system down to the new canonical equilibrium. The non-equilibrium probability distribution for energy changes \( \equiv P_0(\delta E; t_w) \) is peaked at positive energies, with an exponential tail for \( \delta E < 0 \) whose fall-off \( \sim e^{\delta E/2T_{\text{eff}} (t_w)} \) determines the effective temperature. The PES heat-release \( dQ = \delta E \) distribution has been studied, by analytic Monte Carlo (MC) methods for harmonic oscillators\textsuperscript{10} and by numerical MC simulations of spin glasses and Lennard-Jones liquid\textsuperscript{9}.

Equilibration times of supercooled liquids and colloidal crystals\textsuperscript{13,14} rise steeply above a glass temperature \( T_G \), as a Vogel-Fulcher-Tammann (VFT) form \( \sim e^{1/(T - T_G)} \), with unusual time decays and frequency responses\textsuperscript{15}. Although structural glass freezing\textsuperscript{16} that pre-empts crystallization\textsuperscript{17} has been investigated for more than a century, it is still not fully understood. The study of quenches below the solid-solid structural transitions of martensite\textsuperscript{18,19} that also have unusual time evolutions\textsuperscript{11,12} may contribute to an understanding.

Martensites undergo first-order, diffusionless\textsuperscript{3} transitions\textsuperscript{10} from the higher-symmetry austenite, with atomic shifts fixed by their unit-cell distortions (‘military transformations’). The order-parameter strains have degenerate lower-symmetry ‘variants’ separated by crystallographically oriented Domain Walls (DW), that can form complex textures in strain, and in strain-coupled functional variables\textsuperscript{20}. A long-standing puzzle\textsuperscript{11,12} is that while austenite quenched to below an (athermal) martensite start temperature \( M_s \) results in sudden martensitic conversions, quenches to above \( M_s \), show slow conversions instead of no conversions. When \( T \) increases by a few percent closer to a delay divergence temperature \( T_d \), the delays rise sharply from a few, to ten thousand seconds\textsuperscript{12}. To be more relevant for actual experiments, we consider simulations in three dimensions with vector order parameters, such as in the cubic-tetragonal (CT) transition\textsuperscript{12}. There is a two-component strain order parameter \( N_{OP} = 2 \), with three competing unit-cell ‘variants’ \( N_V = 3 \). (Using this notation, the Ising model has \( N_{OP} = 1, N_V = 2 \).)

In this Letter we study the equilibration of 3D athermal martensites for four structural transitions in MC simulations, confirming the generic PES, and its effective...
The temperature that regulates heat release is \( T_w \). We apply PES ideas to quenches across a first order transition. The Order Parameter (OP) rises from zero, enabling the waiting time \( t_w \) to be defined by rising-OP marker events, dependent on \( T \). This choice, \( t_w = t_m(T) \), induces quench temperature dependences in PES distributions: \( T_{eff}(t_w) \to T_{eff}(T) \) and \( P_0(\delta E;t_w) \to P_0(\delta E,T) \). For passages to lower energy shells, as in Fig 1, the OP evolution must satisfy \( T \)-controlled, delay-inducing passage constraints, postulated as of two possible types: a) A constraint that OP configurations must find and enter a Golf Hole (GH) that funnels into fast passage, as inspired by facilitation models; b) A constraint that the OP states must encounter transient catalysts that enable fast passages, as inspired by facilitation models.

Our case is a), and we find a linear vanishing \( T_{eff}(T) \to (T_d - T) \). The ‘search freezing’ temperature \( T_d \) occurs at a pinch-off of the \( \vec{k} \)-space inner radius of a modulated GH. Equilibration times are exponential in entropy barriers, and hence show divergences of the VFT form \( t_m(T) \sim e^{1/T_{eff}(T)} \sim e^{1/(T-T_w)} \). Conversely, entropy barriers vanish and delay times collapse, when the GH is comparable to the Brillouin zone. The predicted divergence \( \sim \) of collapse of conversion times is confirmed by data extracted from simulations and from experiment.

The four chosen structural transition events occur in materials with useful functionalities. The transitions are: tetragonal-orthorhombic (YBCO, superconductivity); cubic-orthorhombic (BaTiO, ferroelectrics); cubic-trigonal (LaSrMnO, colossal magnetoresistance).

To plausibly link simulations to experiment, we must show the model Hamiltonians come from material symmetries. The discretized-strain Hamiltonian in 3D is obtained from a crystal-symmetry invariant strain free energy \( F \), that has physically required Compatibility.

Ginzburg and Landau terms in \( F/E_0 = \sum_{\ell,\ell'} f_{\ell,\ell'} + \sum_{\ell}[f_G + f_L] \). There are six independent physical strain in 3D, that are linear combinations of Cartesian-component strains: compressional \( e_1 \), deviatoric or rectangular \( e_2, e_3 \), and shear \( e_4, e_5, e_6 \). The OP of the \( N_{op} \) = 2 cubic-tetragonal (CT) transition are two deviatoric strains \( \vec{e} = (e_3, e_2) = (\frac{1}{\sqrt{6}}(e_{xx} + e_{yy}) - 2e_{zz}, \frac{1}{\sqrt{3}}(e_{xx} - e_{yy}) \) of the variants. The austenite phase is \( \vec{e} = 0 \).

The remaining \( 6 - N_{op} \) non-OP strains (one compressional and three shears) enter the Hamiltonian as harmonic energies. These are minimized subject to a linear St Venant Compatibility constraint that says no dislocations are generated: the double-curl of the strain tensor must vanish. There are three independent algebraic equations in \( \vec{k} \) space, connecting OP and non-OP strains. The non-OP harmonic energies then analytically yield an OP-OP interaction, whose transition-specific, anisotropic Compatibility kernel is a 2x2 matrix, \( U_{\ell\ell'}(\vec{k}) \) where \( \ell, \ell' = 2, 3 \). There is a prefactor of \( (1 - \delta_{\ell\ell'}) \), and dependence on direction \( \vec{k} = \vec{k}/|\vec{k}| \).

The Landau free energy for CT is \( f_L(\vec{e}) = |(\tau - 1)\vec{e}|^2 - 2(e_3^2 - 3e_3e_2^2) + \vec{e}^2 \) and has 4 minima, at \( N_v = 3 \) variants plus zero strain. Here \( e_x = T(T - T_c)/(T_0 - T_c) \) and \( \tau(T_c) = 0 \) at the spinodal \( T_c \), while \( \tau(T_0) = 1 \) at the first-order transition temperature, that is scaled to be unity \( T_0 = 1 \). The characteristic temperatures in decreasing order are \( T_0 = 1 > T_d > T_c > M_s \). In polar coordinates \( \vec{e} = |\vec{e}|\vec{S} \). Here the unitmagnitude ‘variant vectors’ \( \vec{S}(\vec{r}) \) specify the unit-cell variants on either side of a Domain Wall (DW) that can be martensite-martensite or martensite-austenite. The nonzero \( N_v = 3 \) martensite-variants have spin.
The degenerate Landau minima are at mean-OP magnitudes \( \bar{\varepsilon}(T) = (3/4)(1 + \sqrt{1 - (8\pi)^2/9}) \). The variant domains have mostly-flat strain magnitudes, approximated by \( \bar{\varepsilon}(T) \). Substituting \( \bar{\varepsilon}(T) \to \bar{\varepsilon}(T) \hat{S}(\hat{r}) \), the Landau term becomes \( f_L(\varepsilon) \to f_L(\varepsilon) \hat{S}(\hat{r})^2 \). Here \( f_L(\varepsilon) = \varepsilon(T)^2 g_L(T) \leq 0 \), where \( g_L = (\tau - 1) + (\varepsilon(T) - 1)^2 \leq 0 \). At \( T = T_\infty \), the OP is unity \( \bar{\varepsilon} = 1 \) and \( g_L = 0 \).

Notice a natural separation of response time scales to \( T \) quenches: the OP magnitude \( \bar{\varepsilon}(T) \) responds immediately, while Domain Walls evolve in hundreds or thousands of quenches: the OP magnitude \( \bar{\varepsilon}(T) \) becomes \( \beta H \) term in the Appendix of Ref 15.

At \( \beta H \) term becomes \( \beta H \) term of energy changes. The compatibility term \( \beta H_c > 0 \) has an anisotropic kernel that orients the Domain Walls\(^{14,19,21}\). The \( \ell = \ell' \) kernel \( U_{\ell,\ell}(\hat{k}) \) has a minimum value \( U_{\ell,\ell}(\text{min}) = 0 \) for the most favoured orientation, and a maximum value \( U_{\ell,\ell}(\text{max}) \) for most disfavoured. The kernels for the four 3D transitions are in the Appendix of Ref 15.

In MC simulations, the initial state \( t = 0 \) is high-temperature austenite that is randomly and dilutely seeded with martensite unit-cells. Typical parameters are \( T_0 = 1; \xi_1^2 = 1; T_c = 0.81; E_0 = 3; \) system volume \( L^3 = 16^3; N_{\text{runs}} = 100; \) and holding times \( t_h = 10^4 \) MC sweeps. The martensite fraction is \( n_m(t) = 1/\sum_{\bar{x}} S^2(\bar{r}, t) \leq 1 \), with \( n_m = 0 \) or 1 for uniform austenite or martensite. The conversion time \( t_m \) is defined as when \( n_m(t_m) = 1/2 \). An athermal martensite droplet or embryo can form anywhere, and after waiting for \( t_w = t_m \), can propagate rapidly to the rest of the system\(^{18}\). Hence it is mean rates \( \bar{r}_m \) (or inverse times), that are averaged over runs, analogous to total resistors in parallel determined by the smallest resistance. Mean times \( t_m \) are inverse mean rates: \( t_m(T) \equiv 1/\bar{r}_m(T) \).

The total hamiltonian is \( \beta H = \beta H_C + \beta H_G + \beta H_L \), without extrinsic disorder. It is diagonal in Fourier space,

\[
\beta H = \frac{D_0}{2} \sum_{\ell,\ell'} \sum_{\hat{k}} \epsilon_{\ell,\ell'}(\hat{k}) \hat{S}_\ell(\hat{k}) \hat{S}_{\ell'}(\hat{k}),
\]

with \( D_0 \equiv 2\bar{\varepsilon}(T)^2 E_0/T \). The spectrum, with \( K_{\mu}(\hat{k}) \equiv 2\sin(\mu k/2) \) and \( \mu = x, y, z \), is

\[
\epsilon_{\ell,\ell'}(\hat{k}) \equiv \{g_L(T) + \xi_1^2 \bar{K}^2\} \delta_{\ell,\ell'} + \frac{A_1}{2} U_{\ell,\ell}(\hat{k}).
\]

The Landau term \( H_L \sim g_L < 0 \) and the Ginzburg term \( H_G \approx \bar{K}^2 > 0 \) have competing signs. The Compatibility term \( \beta H_C > 0 \) has an anisotropic kernel that orients the Domain Walls\(^{14,19,21}\). The \( \ell = \ell' \) kernel \( U_{\ell,\ell}(\hat{k}) \) has a minimum value \( U_{\ell,\ell}(\text{min}) = 0 \) for the most favoured orientation, and a maximum value \( U_{\ell,\ell}(\text{max}) \) for most disfavoured. The kernels for the four 3D transitions are in the Appendix of Ref 15.

The MC procedure is standard, but with a crucial extra data retention\(^{18,21}\) of energy changes.

0. Take \( N = L^3 \) sites, each with a vector spin of \( N_{\text{OP}} \) components, in one of \( N_{\text{V}} + 1 \) possible values (including zero) at MC time \( t \). Each \( \{\hat{S}(\hat{r})\} \) set is a ‘configuration’.

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

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

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

4. We collect\(^{22}\) all \( \{\delta E\} \) from each spin-flip (configuration change) within each MC sweep of every run, for all times up to \( t_w \leq t_m(T) \leq t_h \). The set size \( N \times t_m \times N_{\text{run}} \) has up to \( 16^3 \times 10^4 \times 100 \) data points. We take six
quenches, from $T = T_d$ upwards towards $T_d$.

Figure 2a shows $n_m(t)$, the martensite conversion-fraction in a single run, versus MC time $t$ for different temperatures $T$. For quenches $T < T_1$, avalanche conversions, characteristic of athermal martensite, occur in the very first sweep over all spins ($t = 1$). We identify $T_1$ with the martensite start temperature [11,12], $M_s = T_1$. For higher temperatures $T > T_1$, there is a curious ‘incubation’ period when seemingly nothing happens, until a waiting time $t_w = t_m$, brings on a postponed avalanche. Fig 2b shows that the mean incubation delays rise steeply, as $T$ approaches a temperature $T_d$.

Funnels [15] to understand the conversion delays. Suppose a protein model in terms of ball-spring-hinge variables is diagonalized in eigen-modes with eigen-labels $\vec{\alpha}$ and energy spectrum $\epsilon(\vec{\alpha})$. Then $\epsilon(\vec{\alpha}) = 0$ in $\vec{\alpha}$-space defines a zero-energy Golf Hole (GH) contour, with a negative-energy Funnel region inside it. An isotropic spectrum $\epsilon(|\vec{\alpha}|) = 0$ yields a spherical-surface GH, as in a protein folding model [12] with a three-component $\vec{\alpha}$.

For our model, setting the spectrum equal to zero $\epsilon_{\text{eff}}(\vec{k}) = 0$ defines an anisotropic surface in $\vec{k}$-space that is the boundary of the 3D GH. For the CT case, a [1,1,1] slice intersects the GH surface as an open, butterfly-shaped locus with an inner and outer radius, inside the Brillouin Zone (BZ). See Fig 3. The outer radius has $k_{\text{out}}(T)^2 = |g_L(T)|$, that vanishes at $T = T_0$, when the GH is a point. For $T \leq T_1$, the radius $k_{\text{out}}(T)$ is larger than a BZ scale $\sim \pi$, and martensitic passages are immediate. The inner radius has $k_{\text{in}}(T)^2 = |g_L(T)| - (A_1/2)\mathcal{U}_{\ell}(\text{max})$, that pinches off at a $T_d < T_0$ where the GH changes to a segmented four-petaled flower. Passages are energetically open, but topologically blocked. Lower-energy PES shells are available, but not accessible.

We collect the $O(1)$ changes $\{\delta E\}$ to the $O(N)$ energy $E$. The probability $P_0(\delta E, T)$ to access $E' \not\in E$, is proportional to the number of target states $\Omega(E')$. With $S(E') = \ln \Omega(E')$, the probability ratio $R_0(\delta E)$ of energy changes is related to the entropy change $\Delta S(\delta E) \equiv S(E') - S(E) < 0$ by a fluctuation relation for aging [14]:

$$R_0 \equiv P_0(\delta E, T)/P_0(-\delta E, T) = \Omega(E')/\Omega(E) = e^{\Delta S(\delta E)}. \tag{3}$$

Entropy barriers $S_E \equiv -\Delta S$ rise, when the searched-for states become rarer (key seeks lock, most attempts fail). Since $R_0(\delta E)R_0(-\delta E) = 1$, the entropy change is odd, $\Delta S(\delta E) + \Delta S(-\delta E) = 0$, and a solution is

$$P_0(\delta E, T) = P_0(\delta E, T) e^{\frac{1}{2}\Delta S(\delta E)}, \tag{4}$$

with an even $P_0(\delta E, T) \equiv \sqrt{P_0(\delta E, T) P_0(-\delta E, T)}$. The leading term in the entropy-change for small heat releases is $\Delta S \simeq \beta_{\text{eff}}\delta E$ where $\beta_{\text{eff}} \equiv 1/T_{\text{eff}}$. For $\delta E = -|\delta E| < 0$, the Boltzmann-like form $P_0 \simeq e^{-\frac{1}{2}\beta_{\text{eff}}(T)|\delta E|}$ gives a physical meaning to the effective temperature, as a search range of accessible energy shells. If $\beta_{\text{eff}} \to 0$, entropy barriers collapse, and passages are immediate. If $T_{\text{eff}} \to 0$, then entropy barriers diverge, and passages cease. Glassy freezing is a shutdown of PES searches.

Fig 4a shows that, as in PES model [14], the $P_0(\delta E, T)$ peaks at positive $\delta E$, understood as a completion-of-square between a gaussian peaked at the origin and an exponential tail for $\delta E < 0$. Fig 4b shows behaviour near the origin, where the slopes define $\frac{1}{2}\beta_{\text{eff}}(T)$.

Fig 5 shows the dependence of $\beta_{\text{eff}}(T)$ and $T_{\text{eff}}(T)$ on the quench temperature $T$. The data suggest there is a linear vanishing of $T_{\text{eff}}(T) \simeq (1/B_0)|T - T_d|$ near a search freezing at $T_d$, and also a vanishing of $\beta_{\text{eff}} \sim |T - T_1|$ near a search avalanche at $T_1$.
Fig 6 shows log-linear plots for a scaled $\Pi_0(\delta E,T) \equiv P_0(\delta E,T)/P_0(0,T)$ versus the entropy-barrier related variable $1/\beta_{eff} \delta E$. See also Figure insets, Ref 4. Data are for four 3D structural transitions, and six $T$ between the collapse and divergence of entropy barriers.

If the mean conversion time is exponential in the entropy barrier, then near $T_d$ we have $t_m(T) \simeq t_0 e^{-B_0/\delta_0(T)}$, where the constants $B_0, t_0$ can be fixed by simulational and experimental data\(^a\). The initial slope in $|\delta_0|$ of $1/\ln t_m(T)$ gives $1/B_0$; and the extrapolated intercept of ln $t_m(T)$ versus $1/|\delta_0(T_0)|$ gives $t_0$. For Ni-Al data\(^b\) the ‘fragility’ parameter $B_0 T_d = 1.23$ Kelvin, and the austenite-martensite DW time scale is $t_0 = 1$ sec.

Fig 7a shows that CT times show VFT behaviour near $T_d$ and fall-off behaviour near $T_1$. Fig 7b shows data extracted from Ni-Al and Fe-Al alloys\(^1\)\(^2\)\(^3\)\(^4\)\(^5\).

In summary, post-quench aging in athermal martensites shows characteristic signatures of the Partial Equilibrium Scenario. The VFT behaviour found in 3D simulations/ experiments is understood as a consequence of a linearly vanishing PES search temperature.

Further model simulations under deeper quenches could study if facilitation constraints of vanishing lifetimes of transient catalyst\(^6\)\(^7\) could induce DW glass freezing. Further experimental work on martensitic alloys\(^1\)^4 could record signal and noise under systematic quench steps of $1/|\delta_0|$, over the delay region $T_d > T > T_1$; as well as the precursory\(^1\)^4 region $T_0 > T > T_d$ above it. The distributions of intermittent energy releases could be measured through their concurrent resistive, photonic, acoustic, and elastic signals\(^1\)^2\(^3\)\(^4\). Finally, quenches of complex oxides\(^1\)\(^2\)\(^3\) near their structural/ functional transitions, might similarly induce\(^1\) PES aging in their (strain-coupled) functional variables.

Acknowledgement: It is a pleasure to thank Smarajit Karmakar for valuable discussions on the glass transition.

---

1. F. Ritort, J. Phys. Chem. B 108, 6893 (2004); and in Unified Concepts in Granular Media and Glasses, (eds.) A. Coniglio, A. Fierro, H.J. Hermann and M. Nicodemi, Elsevier (2004); arXiv/ condmat/ 03113710v1.
2. A. Crisanti and F. Ritort, Europhys. Lett., 66, 253 (2004).
3. L. L. Bonilla, F.G. Padilla and F. Ritort, Physica A 250, 315 (1998);
   L. Garriga and F. Ritort, Phys. Rev. E 72, 031505 (2005).
4. A. Crisanti, M. Pecco and F. Ritort, Phys. Rev. Lett., 110, 080601 (2013).
5. K. Binder, W. Kob, Glassy Materials and Disordered Solids, World Scientific, Singapore (2005); A.L. Greer, K.F. Kelton, S. Sastry, Eds., Fraility of glass-forming liquids, Hindustan Book Agency, New Delhi (2014). A VFT time $\sim e^{1/(T-T_c)}$ written as $e^{E_G(T)/T}$ suggests a diverging activation energy barrier. Written as $e^{-\Delta S(T)} \sim e^{1/T_{eff}(T)}$ it suggests a diverging entropy barrier through the linear vanishing of an effective temperature, from a closing bottleneck.
6. P. Harrowell, Nature Phys 2, 157 (2006); H. Shintani and H. Tanaka, Nature Phys 2, 200 (2006); X. Yang, H. Tong, W-H. Wang, and K. Chen, Phys. Rev. E, 99, 062610 (2019).
7. P. Lunkenheimer, S. Kastner, M. Koehler and A. Loidl, Phys. Rev. E 81, 051504 (2010).
8. R. Boehmer, K.L. Ngai, C.A. Angell, D.J. Plazek, J. Chem. Phys., 99, 4201 (1993); T.V. Ramakrishnan and M. Raj Lakshmi, Eds., Non-Debye relaxation in condensed matter, World Scientific, Singapore (1987).
9. H. Fang, M.F. Hagan, W.B. Rogers, Proc. Nat. Acad. Sci., 117, 27927 (2020).
10. K. Bhattacharya, Microstructure of Martensite, Oxford University Press (2003).
11. T. Kakeshita, T. Fukuda and T. Saburi, Scripta Mat. 34, 1 (1996); T. Kakeshita, K. Kuroiwa, K. Shimizu, T. Ikeda, A. Yamagashi, and M. Date, Mat. Trans. JIM, 34, 423 (1993).
12. M. Aspelmeyer, U Klemradt, L.T. Wood and S.C. Moss, Phys. Stat. Sol. (a) 174, R9 (1999); L. Müller , U. Klemradt, T.R. Finlayson, Mat. Sci. and Eng. A 438, 122 (2006); L. Müller, M. Waldorf, G. Gutt, G. Grubel, A. Madsen, T. R. Finlayson and U. Klemradt, Phys. Rev. Lett., 109,105701 (2011).
13. P.R. Rios and J.R.C. Guimaraes, Scripta Mat., 57, 1105 (2007); P.R. Rios, F.G. Cardoso, T.A. Neves and J.R.C. Guimaraes, in the Minerals, Metals and Materials Society, TMS 2015 144th Annual Meeting, Cham, Springer (2015), https://doi.org/10.1007/978-3-319-48127-2_84.
14. S. Kartha, J. A. Krumhansl, J. P. Sethna, and L. K. Wickham, Phys. Rev. B 52, 803 (1995).
15. S.R. Shenoy, T. Lookman and A. Saxena, Phys. Rev. B 82, 144103 (2010). See Appendix for the four Compatibility kernels in 3D.
16. K.O. Rasmussen, T. Lookman, A. Saxena, A.R. Bishop, R.C. Albers and S.R. Shenoy, Phys. Rev. Lett., 87, 055704 (2001).
17. N. Shankaraiah, K. P. N. Murthy, T. Lookman and S. R. Shenoy, Europhys. Lett. 92, 36002 (2010); Phys. Rev. B 84, 064119 (2011); Phys. Rev. B 91, 214108 (2015).
18. W.I.F. David,C.C. Wilson, P. P. Edwards, R. Jones, M.R. Harrison, Nature 331, 245 (1988); V. Hardy, A. Maignan, S. Hebert, C. Yaicle, C. Martin, M. Hervieu, M.R. Lees, G. Rowlands, D. McK. Paul and B. Raveau, Phys. Rev. B 68, R220402 (2003); V. Hardy, S. Majumdard, S.J. Crowe, M.R. Lee, D. McK. Paul, L. Herve’, A. Maignan, S. Hebert, C. Martin, C. Yaicle, M. Hervieu and B. Raveau, Phys. Rev. B 9, 020407 (R) (2004); V. Podzorov, B.G. Kim, V. Kryukin, M.E. Gershenson and S.W. Cheong, Phys. Rev. B 64, 140406 (R) (2001); V Podzorov, C.H. Chen, M.E. Gershenson and S-W. Cheong, Europhys. Lett., 55, 411 (2001).
19. D. J. Bicout and A. Szabo, Protein Science 9, 452 (2000); P.G. Wolynes, Proc. of the Am. Phil. Society 145, 4 (2001); M. Cleplak and J.I. Sulkowska, J. Chem. Phys.,123,194908
Supplementary Material. [ URL]

Videos for the 2D square-rectangle $N_{OP} = 1, N_V = 2$ transition, with austenite (green) and the two martensite variants (red/ blue), show sequentially evolving Domain Wall phases, from DW Vapour to DW Liquid to DW Crystal or oriented ‘twins’. The 3D physical picture is similar, but we show the earlier 64$^2$ 2D system as illustrations.

Video A. The droplet in $\vec{r}$-space: This shows the coordinate-space evolution for $T_d > T > T_1$, for the Golf Hole type a) passage of Fig 1. Random initial martensite seeds rapidly form a single-variant DW Vapour droplet, enclosed in a martensite-austenite DW. This fluctuates like an amoeba, searching over incubation delays for a conversion passage to a DW Liquid, and then a quick symmetry-breaking to a DW crystal.

Video B. The droplet in $\vec{k}$-space: This shows the evolution as Video A but now in Fourier space, for $T_d > T > T_1$. The dynamic structure factor for variant spins $|S(\vec{k}, t)|^2$ is shown in $(k_x, k_y)$ space, with elliptic contours of a DW Vapour going to the bi-diagonal X of a DW Liquid, and to a single-diagonal $k_y = -k_x$ line of a DW Crystal.

Videos C,D are in different quench regimes than A,B but are also given for completeness. Video C. The $\vec{r}$-space dynamic catalysts: This shows the evolution for deep quenches to $T << T_1$, of the facilitation type b) passage. The DW Vapour now converts rapidly to a sluggish DW Liquid of frozen walls. Transient hotspots of austenite in martensite act as dynamic catalysts, that unlock and delete even far-off minority-diagonal DW segments, leaving a dominant-diagonal ,martensite-martensite DW crystal, or twins.

Video D. The $\vec{r}$-space tweed precursor: This shows dynamical tweed in the above-transition region $T > T_d > T_1$, of an oscillating array of martensitic islands in austenite sea. This might arise from a vibrating $\vec{k}$ space profile of the droplet, attempting to enter a topologically blocked GH .

S. R. Shenoy and T. Lookman, Phys. Rev. B 78, 144103 (2008), see Fig 7.

N. Shankaraiah, K.P.N. Murthy and S.R. Shenoy, unpublished.

Another $N_{OP} = 2, N_V = 3$ kernel in 2D reproduces the self-similar star textures of lead orthovanadate. R. Vasseur, T. Lookman and S.R. Shenoy, Phys Rev B 82, 094118, 92010 (2010); C. Manolikas and A. Amelinckx, Phys. Stat. Sol., 60, 607 (1980); 61, 179 (1980).

U. Chandni, S Kar-Narayan, A. Ghosh, H.S. Vijaya and S. Mohan, Acta Mater., 57, 6113 (2009); A. Planes, Ll. Manosa and E. Vives, J. Alloys and Comp., 577, S699 (2013);
X. Balandraud, N. Barrara, P. Biscarin, M. Grediac, G. Zanzotto, Phys. Rev. B, 91, 174111 (2015); B. Blaysat, X. Balandraud, M. Grediac, E. Vives, N. Barrera and G. Zanzotto, Nature Commun. Mater., 1, 3 (2020); Z. Eranson, B. Ruta, S. Hechler, M. Stolpe, E. Pineda, I. Gallimo, and R. Busch, Phys. Rev. Lett., 115, 175701 (2015). See also Physics 8, S5121 (2015).