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

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We do Monte Carlo simulations of four 3D structural transitions, with vector-spin models of their martensitic strain domains under quenches to $T$, to test a generic post-quench Partial Equilibration Scenario (PES) of Ritort. We indeed confirm that energy-lowering passages between fixed-energy shells induce a signature PES distribution of 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 PES passage-searches freeze, explains the Vogel-Fulcher like divergence of equilibration times $e^{1/T_{\text{eff}}(T)} \sim e^{1/(T_d-T)}$, extracted from incubation-time delays of simulations and martensitic alloys.

Glassy freezing or structural arrest of a rapidly cooled liquid or colloidal system\textsuperscript{5,10} that pre-empts crystallisation, has been investigated for more than a century. Supercooled liquid models can yield heterogeneous domains of competing crystal structures\textsuperscript{11–16}. Equilibration time divergences at a glassy freezing temperature $T_G$, have been fitted to Vogel-Fulcher-Tammann (VFT) $\sim e^{1/T-T_G}$, or other forms\textsuperscript{17}. It is natural to study generic equilibration scenarios\textsuperscript{18} in specific structural-domain systems that have long relaxation times\textsuperscript{11,15,16}.

After a sudden quench, a system on a free energy landscape, has competing pathways to the new global minimum, delayed by free energy barriers $\{\Delta F = \Delta U - T\Delta S\}$. The delay rates $e^{-\Delta F/T}$ will be from energy barriers ($\sim e^{-\Delta U/T}$) and entropy barriers ($\sim e^{-\Delta S}$), schematically depicted in Fig 1. Ritort and colleagues\textsuperscript{2,4,19} have proposed a Partial Equilibration Scenario (PES) of Ritort. We indeed confirm that energy-lowering passages between fixed-energy shells induce a signature PES distribution of 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 PES passage-searches freeze, explains the Vogel-Fulcher like divergence of equilibration times $e^{1/T_{\text{eff}}(T)} \sim e^{1/(T_d-T)}$, extracted from incubation-time delays of simulations and martensitic alloys.

![FIG. 1. Schematic of delays from two limits of free energy barriers. a) Energy-barrier delays from thermally activated jump attempts. b) Entropy-barrier delays from searches for rare passages. Key seeks lock, most attempts fail.](image)

In this Letter we do MC simulations in three dimensions, with vector order parameter strains, for four structural transitions\textsuperscript{18}. We present here the cubic-tetragonal (CT) transition\textsuperscript{15}, with a strain order parameter of components $N_{OP} = 2$, with three competing unit-cell `variants' $N_V = 3$. We confirm for all four transitions, that the PES energy change distribution has the predicted generic behaviour: an exponential tail, with an effective...
temperature that regulates heat release.\footnote{\bibitem{5}B\bibitem{19}}

For our specific case of 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 at $t_m$, that depend on $T$. This choice $t_w = t_m(T)$ induces quench-temperature dependences: $T_{\text{eff}}(t_w) \rightarrow T_{\text{eff}}(T)$ and $P_0(\delta E; t_w) \rightarrow P_0(\delta E, T)$. For passages to lower energy shells, the OP evolution must satisfy $T$-controlled entropy-barrier constraints, postulated as of two types: a) A constraint that OP configurations must find and enter a Fourier space bottleneck that is like a Golf Hole (GH) that funnels into fast passage, as suggested for protein folding\footnote{\bibitem{19}B\bibitem{19}} or b) A constraint that the OP states need transient catalysts to enable fast passages, as inspired by facilitation models\footnote{\bibitem{19}B\bibitem{19}}. Our case is a), and we find a linear vanishing $T_{\text{eff}}(T) \sim (T_d - T)$. The ‘search freezing’ temperature $T_d$ occurs at a pinch-off on warming, of the $\mathbf{k}$-space inner radius of an angularly modulated bottleneck. Equilibrium times are exponential in entropy barriers, and for quenches $T_d > T > T_1$, diverge as $t_m(T) \sim e^{1/T_{\text{eff}}(T)} \sim e^{1/(T_d - T)}$. Thus VFT-like behaviour is not restricted to the glass transition. Conversely, entropy barriers vanish and delay times collapse for $T < T_1$, when the bottleneck expands on cooling to span the Brillouin zone.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{Delay times for CT martensitic conversion: The martensite fraction $n_m(t_m) = 0.5$ defines $t_m$. a) For $T \leq T_1$ avalanche conversions occur, at $t_m = 1$. For $T > T_1$ DW sluggishness causes 'incubation' delays or postponement of conversion avalanches to $t = t_m(T)$. b) Log-linear plot of mean delay time $t_m(T)$ versus $T/T_d < 1$. Delay times are not exponentially sensitive to Hamiltonian energy scales $E_0$, so are not activated: delays are from entropy barriers.}
\end{figure}

We derive a discretized-strain Hamiltonian\footnote{\bibitem{19}B\bibitem{19}} in 3D, from a crystal-symmetry invariant strain free energy $F$, that has Compatibility\footnote{\bibitem{19}B\bibitem{19}} Ginzburg, and Landau terms in $F/E_0 = \sum_{\tau,\rho} f_{\tau} + \sum_{\ell} f_{G} + f_{L}$, with $E_0$ an energy scale. There are six independent physical strain tensors\footnote{\bibitem{19}B\bibitem{19}} in 3D, that are linear combinations of Cartesian tensor strains: compressional $\varepsilon_1$; deviatoric or rectangular $\varepsilon_2, \varepsilon_3$, and shear $\varepsilon_4, \varepsilon_5, \varepsilon_6$. The OP of the cubic-tetragonal (CT) transition are two deviatoric strains $\bar{\varepsilon} = (\varepsilon_1, \varepsilon_2) = (\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}, \sqrt{\frac{1}{2}} (\varepsilon_{xx} - \varepsilon_{yy}))$. Austenite is $\bar{\varepsilon} = 0$.

The remaining $6 - N_{\text{OP}}$ non-OP strains (one compressional and three shears) enter the Hamiltonian as harmonic springs. These are minimized subject to a linear St Venant Compatibility constraint\footnote{\bibitem{19}B\bibitem{19}} that says no dislocations are generated: the double-curl of the strain tensor must vanish. There are three independent algebraic equations in $\mathbf{k}$ space, connecting OP and non-OP strains\footnote{\bibitem{19}B\bibitem{19}}. The harmonic non-OP strains then analytically yield an OP-OP interaction, whose transition-specific, anisotropic Compatibility kernel\footnote{\bibitem{19}B\bibitem{19}} is a $2 \times 2$ matrix, $U_{\ell,\ell'}(\mathbf{k})$ where $\ell, \ell' = 2, 3$. There is a prefactor of $(1 - \delta_{E,0})$, and dependence on direction $\mathbf{k} = \mathbf{k}/|\mathbf{k}|$.

The Landau free energy for CT is $f_L(\varepsilon) = (T - 1)e^2 - 2(e_3^2 - 3e_3e_2^2) + \varepsilon^4$ and has 4 minima, at $N_V = 3$ variants plus at zero strain. Here $\tau(T) \equiv (T - T_0)/(T_0 - T_c)$, and $\tau(T_c) = 0$ at the spinodal $T_c$, while $\tau(T_0) = 1$ at the first-order transition temperature, scaled to be unity $T_0 = 1$.

In ‘polar’ coordinates, $\bar{\varepsilon} \equiv |\varepsilon| \bar{S}$. Here the unit-magnitude ‘variant vectors’ $\bar{S}(\bar{r})$ 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\footnote{\bibitem{19}B\bibitem{19}} $S = (S_3, S_2) = (1, 0), (-1/2, \sqrt{3}/2), (-1/2, -\sqrt{3}/2)$, pointing to corners of an equilateral triangle in a unit circle, while the centroid $\bar{S} = (0, 0)$ is austenite. Thus $S^2 = 0$ or 1.

The degenerate Landau minima are at mean-OP magnitudes $\bar{\varepsilon}(T) = (3/4) [1 + \sqrt{1 - (8\tau/9)}]$. The variant domains have mostly-flat strain magnitudes, approximated by $\bar{\varepsilon}(T)$. Substituting $\bar{\varepsilon}(\bar{r}) \rightarrow \bar{\varepsilon}(T) \bar{S}(\bar{r})$, the Landau term becomes $f_L(\bar{\varepsilon}) \rightarrow f_L(T) \bar{S}(\bar{r})^2$. Here $f_L(T) = \sum_{\ell,\ell'} U_{\ell,\ell'}(\mathbf{k})$. The phase diagram is plotted in FIG. 2.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.png}
\caption{Bottlenecks in Fourier space for CT transition: The temperature dependence of bottleneck size and shape is shown for a [1,1,1] slice of a 3D anisotropic bottleneck. a) The 2D slice in $\mathbf{k}$. Anisotropic ‘Golf Hole’, enclosing negative martensite states, that shrinks with warming $T$. The outer butterfly shape changes topology to a segmented four-petal flower shape at $T = T_d$. b) The anisotropic bottleneck inner and outer radii $k_{\text{in}}, k_{\text{out}}$ are plotted vs $T$. The bottleneck outer radius $k_{\text{out}}(T)$ for $0 < T \leq T_1$ (arrow) spans a Brillouin Zone size of $\sim \pi$ (horizontal light dashes), so conversions are immediate. The outer radius shrinks to a point on the right at the thermodynamic transition $T = T_0 = 1$ to austenite-only states. On the other hand, the inner radius $k_{\text{in}}(T)$ shrinks on warming for $0 < T < T_d$, vanishing (arrow) at $T = T_d$ when the outer radius is still nonzero: the bottleneck topology changes.}
\end{figure}
\( \varepsilon(T)^2 g_L(T) \leq 0 \), where \( g_L = (\tau - 1) + (\varepsilon(T) - 1)^2 \leq 0 \). At \( T = T_h^- \), the OP is unity \( \varepsilon = 1 \) and \( g_L = 0 \).

Notice a separation of time scale responses to \( T \) quenches: the OP magnitude \( \varepsilon(T) \) responds immediately, at \( t = 1 \), while Domain Walls can take thousands of time steps \( t \), to evolve successively from DW Vapour to DW Liquid to a DW Crystal of twins. For our case of shallow quenches \( T_d > T > T_1 \), it is the DW Vapour-to-Liquid conversion has the long (bottleneck type) delays studied here. See Videos A.B. The DW moves by correlated flips of spins that bracket it, while domain spins remain locked: a dynamical heterogeneity in space and time. [For deeper quenches \( T_1 \ll T_1 \) not studied here, it is the DW Liquid-to-Crystal twin orientation that has long (facilitation type) delays. See Video C.]

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

\[
\beta H = \frac{D_0}{2} \left[ \sum_{\ell,\ell'} \sum_{\kappa} \epsilon_{\ell,\ell'}(\kappa, T) \bar{S}_\ell(\kappa) \bar{S}_{\ell'}(\kappa) \right],
\]

with \( D_0 = 2\varepsilon(T)^2 E_0/T \). The spectrum, with \( K_\mu(\kappa) \equiv 2 \sin(k_\mu/2) \) and \( \mu = x, y, z \), is

\[
\epsilon_{\ell,\ell'}(\kappa, T) \equiv \{ g_L(T) + \xi^2_0 \kappa^2 \} \delta_{\ell,\ell'} + \frac{A_1}{2} U_{\ell\ell'}(\kappa).
\]

The anisotropic Compatibility kernel in the energy spectrum can induce preferred DW orientations. For example the \( \ell = \ell' \) kernel \( U_{\ell,\ell}(\kappa) \) is smallest \( \bar{U}_{\ell,\ell}(\kappa) = 0 \) at the most favoured orientation, and largest \( \bar{U}_{\ell,\ell}(\kappa) > 0 \) for most disfavoured. The negative sign of the Landau term \( H_L \sim g_L < 0 \) and the positive signs of the Ginzburg term \( H_G \sim \kappa^2 > 0 \) and the Compatibility term \( H_C > 0 \) imply the spectrum \( \epsilon_{\ell,\ell'}(\kappa, T) \) could vanish along some Fourier contour. This contour will be angularly modulated, through the anisotropy of the Compatibility kernel.

In MC simulations, the initial state \( t = 0 \) is high-temperature austenite that is randomly and dilutely (2%) seeded with martensite unit-cells. Typical parameters are \( T_0 = 1; \xi^2_0 = 1; T_c = 0.95; E_0 = 3 \); system volume \( N = L^3 = 16^3 \); \( N_{\text{runs}} = 100 \); and holding times \( t_h = 10^4 \) MC sweeps. The martensite fraction is \( n_m(t) = \frac{1}{N} \sum_{\rho} S^2(\rho, t) \leq 1 \), 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 rapidly form anywhere, and after waiting till \( t_m = t_m \), can propagate rapidly to the rest of the system. 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 MC procedure is standard, but with a crucial extra data retention [42] of energy changes.

0. Take \( N \) sites, each with a vector spin of \( N_{OP} \) components, in one of \( N_r \) possible values (including zero) at MC time \( t \). Each \( \{ \bar{S}(\rho) \} \) set is a ‘configuration’.

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

2. If the energy change \( \delta E \leq 0 \), 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 [23] all \( \{ \delta E \} \) from each spin-flip (configuration change) within each MC sweep of every run, up to the conversion time for that run, \( t \leq t_m(T) \leq t_h \). The set size \( N \times t_m \times N_{\text{runs}} \) has up to \( 16^3 \times 10^4 \times 100 \) data points. We take six quenches, from \( T = T_1 \) up to \( T_d \).

Figure 2a shows \( n_m(t) \), the martensite conversion-fraction in a single run, versus MC time \( t \) for different temperatures \( T \). For quenches \( T \leq T_1 \), avalanche con-

![Image](56x442 to 297x556)
versions, characteristic of athermal martensite, occur in the very first sweep over all spins \((t = 1)\). We identify \(T_1\) with the martensite start temperature \([11,12]\). For higher temperatures \(T > T_1\), there is a curious ‘incubation’ period, when nothing happens macroscopically, until a postponed avalanche at \(t_w = t_m\). These models display the delayed transitions and burst-like growth of order, characteristic of martensites and manganites \([11,12]\). Fig 2b shows that for \(T\) above \(T_1\) (downward arrow), and approaching \(T_d\), the mean incubation delays rise steeply, due to entropic bottlenecks.

For our model, the boundary of a 3D bottleneck is from the spectrum set equal to zero \(\varepsilon_{s,\ell}(\bar{k}) = 0\), defining an anisotropic surface in \(\bar{k}\)-space. For the CT case, a \([1,1,1]\) slice can intersect the bottleneck surface as an open, butterfly-shaped locus with an inner and outer radius, inside the Brillouin Zone (BZ). See Fig 3. For \(T \leq T_1\), the radius \(k_{out}(T)\) is larger than a BZ scale \(\sim \pi\), and martensitic passages are immediate. For \(T_1 < T < T_d < T_0\), the butterfly bottleneck shrinks on warming. At \(T = T_d\), the inner squared-radius \(k_{in}(T)^2 = |g_L(T)| - (A/2)U_{\ell,\ell}(\text{max})\) vanishes, and the topology of the connected butterfly changes to that of a segmented four-petaled flower: entropy barriers diverge, and PES heat releases are arrested. For the ‘precursor’ region \([13]\) \(T_d < T < T_0\), PES passages are energetically available, but entropically inaccessible. Repeated bottleneck entry attempts could induce vibrations. See Video D. Finally, at \(T = T_0 = 1\), the outer squared-radius \(k_{out}(T)^2 = |g_L(T)|\) also vanishes: the bottleneck becomes a point, and only austenite exists.

We collect the \(O(1)\) changes \(\{\delta E\}\) to the \(O(N)\) energy \(E\). The probability \(P_0(\delta E, T)\) to access \(E'\) from \(E\), 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 \([14]\):

\[
R_0 = \frac{P_0(\delta E, T)}{P_0(-\delta E, T)} = \frac{\Omega(E')}{\Omega(E)} = e^{\Delta S(\delta E)}. \tag{3}
\]

Entropy barriers \(S_B \equiv -\Delta S > 0\) rise, when the searched-for states become rarer. 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 for the PES distribution is

\[
P_0(\delta E, T) = P_0(\delta E, T) e^{\delta S(\delta E)}, \tag{4}
\]

with an even \(P_0(\delta E, T) = \sqrt{P_0(\delta E, T) P_0(-\delta E, T)}\). The leading entropy-change term for small heat releases is \(\Delta S \equiv \beta_{eff}\delta E\) where \(\beta_{eff} \equiv 1/T_{eff}\). For \(\delta E = -|\delta E| < 0\), the Boltzmann-like form \(P_0 \simeq e^{-\delta_{eff}(T)|\delta E|}\) gives a physical meaning to the effective temperature, as a search range denoting 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 passages cease. Glass-like freezing is a shutdown of PES searches.

Fig 4a shows that, as in PES models \([10]\), the \(P_0(\delta E, T)\) peaks are 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 a zoom-in near the origin, where the slopes define \(\beta_{eff}(T)\).

Fig 5 shows the dependence of \(\beta_{eff}(T)\) and \(T_{eff}(T)\) on the quench temperature \(T\). The data suggest a linear vanishing of \(T_{eff} \simeq (T_d - T)/(B_0T_d)\) near \(T_d\), at a search freezing and a suppression of the heat releases to the bath. There is also a linear vanishing of \(\beta_{eff} \sim T - T_1\) near \(T_1\), at a search avalanche and prompt equilibration.

Fig 6 shows log-linear plots for a scaled \(\Pi(\delta E, T) \equiv P_0(\delta E, T)/P_0(0, T)\) versus the entropy-barrier related
variable $\frac{1}{2} \beta_{eff} \delta E$. Data are for four 3D structural transitions\textsuperscript{13,14} and six $T$ between the collapse ($T_1$) and divergence ($T_d$) of entropy barriers.

The mean conversion time is exponential in the entropy barrier\textsuperscript{23} $\tau \sim e^{1/\delta_{m}(T)}$, so near $T_d$ we have $\tau_m(T) \approx t_0 e^{B_0/|\delta_0(T)|}$, where the constants $B_0, t_0$ can be fixed by simulation and experimental data\textsuperscript{24}. The initial slope in $|\delta_0|/\ln \tau_m(T)$ gives $1/B_0$ and the extrapolated intercept of $\ln \tau_m(T)$ versus $B_0/|\delta_0(T)|$ gives $t_0$. For Ni-Al data\textsuperscript{11} the ‘fragility’ parameter $2B_0 t_0 \cong 1.23$ Kelvin, and the austenite-martensite DW hop time is $t_0 \cong 1$ 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\textsuperscript{11,12} are similar.

Signatures of PES could be sought, in previous simulations or experiments\textsuperscript{13} under systematic temperature quenches, with a recording of energy releases. Further experimental work on martensitic alloys\textsuperscript{11,12} 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 for the precursory\textsuperscript{13,14} region $T_0 > T > T_d$ above it. Non-stationary distributions of energy releases might be determined through concurrent resistive, photonic, acoustic, and elastic signals\textsuperscript{23}. Finally, one might speculate that complex oxides quenched near their structural/functional transitions, could show PES ageing behaviour in their (strain-coupled) functional variable\textsuperscript{13,14}.

In summary, post-quench ageing in athermal martensites shows characteristic signatures of the Partial Equilibration Scenario. The conversion arrest and delay- divergence found in 3D simulations and alloy experiments, are understood as arising from a vanishing of the search temperature that governs the PES cooling process.

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18. The four chosen structural transitions can occur in materials with useful functionalities\textsuperscript{17}. The transitions are: tetragonal-orthorhombic (YBCO, superconductivity); cubic-tetragonal (FePd, shape memory); cubic-orthorhombic (BaTiO\textsubscript{3}, ferroelectrics); cubic-trigonal (LaSrMnO\textsubscript{3}, colossal magnetoresistance).
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Supplementary Material.

Videos for the 2D square-rectangle, $N_{OP} = 1, N_V = 2$ transitions for 64 $\times$ 64 systems, with austenite (green) and the two martensite variants (red/ blue), show sequentially evolving Domain Wall states, from DW Vapour to DW Liquid to DW Crystal or oriented ‘twins’. The 3D physical evolutions are similar.

Video A. The droplet in $\vec{r}$-space: This shows the coordinate-space evolution for $T_d > T > T_1$, for the bottleneck type passage. Random initial martensite seeds rapidly form a single-variant DW Vapour droplet, bounded by 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 $T_d > T > T_1$ evolution as Video A but now in Fourier space. 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.

Video C. The $\vec{r}$-space dynamic catalysts: This shows the evolution for deep quenches to $T < < T_1$, of the facilitation type passage. The DW Vapour now converts rapidly to a sluggish DW Liquid of frozen walls. Transient hotspots of austenite in martensite act as facilitation variables or dynamic catalysts, that unlock and delete even far-off minority-diagonal DW segments, leaving a dominant-diagonal DW crystal, or twins.

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

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 $\sigma^2 = 2MT_{eff}$, the acceptance fraction is a complementary error function, whose asymptotic behaviour yields $t_0/\bar{t} \simeq e^{-M/4T_{eff}}$. Dropping constants, the martensitic mean conversion time near $T_d$ is written simply as $\bar{t}_m(T) = t_0 e^{1/T_{eff}(T)}$. 

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