Depletion of two-level systems in ultrastable computer-generated glasses

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Amorphous solids exhibit quasi-universal low-temperature thermal anomalies whose origin has been ascribed to a distribution of localized tunneling defects. Using an advanced Monte Carlo procedure, we create in silico glasses spanning from hyperquenched to vapor-deposited ultrastable glasses. Using a multidimensional path-finding protocol, we locate tunneling defects with energy splittings smaller than \( k_B T_Q \), with \( T_Q \) the temperature below which quantum effects are relevant (\( T_Q \approx 1 \) K in most experiments). We find that the evolution of the energy landscape with the quench rate, as well as the manner in which the landscape is explored, conspire to deplete the density of tunneling defects in well-annealed glasses, as observed in recent experiments. We systematically explore the real-space nature of tunneling defects, finding that they are mostly localized to the participation of a few atoms, but are occasionally dramatically delocalized.

The theory of low-temperature properties of perfect crystals stands as one of the most profound early tests of the power of quantum statistical mechanics. In particular, Debye’s seminal calculation of the observed \( T^3 \) behavior of the low-temperature specific heat highlighted the importance of long wavelength phonons as low energy excitations in ordered solids [1]. Given that the wavelength of populated phonon modes in the temperature range \( T \sim 1 \) K is significantly longer than the interparticle distance in a typical solid, it came as a major surprise in 1971 when Zeller and Pohl [2] measured large deviations from the expected Debye behavior of the specific heat and the thermal conductivity of vitreous silica and other selenium and germanium-based glasses. An explanation for this puzzling behavior was almost immediately put forward by Anderson, Halperin and Varma [3] and by Phillips [4]. They posited that, due to the disorder intrinsic to amorphous solids, the energy landscape of a glass contains many local minima. Rare, nearly degenerate, adjacent local minima support tunneling defects or two-level systems (TLS) with energy splittings of the order of 1 K, which provide a large excess contribution to the specific heat and a new mode of scattering that determines the thermal conductivity. In the subsequent decades, the generic behavior described by Zeller and Pohl has been observed in numerous other amorphous materials, and the TLS theory has withstood essentially all experimental tests [5–9]. Despite this great progress in our understanding, the microscopic real-space structure of the tunneling defects remains debated, as do the factors that determine the density and distribution of TLS in amorphous solids [10–22].

A powerful platform for addressing the aforementioned issues is the use of computer simulation to prepare amorphous materials in silico and to interrogate the simulated energy landscape for TLS in an ab initio manner [23]. Such a program was initiated in the pioneering work of Heuer and Silbey nearly three decades ago [24–27]. Limited by the computational power and the algorithms available at the time, they created model glasses formed with cooling rates roughly nine orders of magnitude larger than those found in the laboratory setting, and were able to locate only a handful of TLS with the requisite tunnel splittings, necessitating uncontrolled extrapolations. In the subsequent years the situation has incrementally improved [28–30], although until very recently the algorithmic ability to simulate amorphous materials which are cooled in an experimentally realistic fashion has remained completely out of reach. This obstacle has greatly limited the ability to microscopically understand the universal anomalous thermal behavior of low-temperature amorphous solids from a computational viewpoint.

In this work we leverage the remarkable ability of the swap Monte Carlo algorithm to produce in silico amorphous materials with quench rates that range from those found in typical experiments to the significantly slower rates found in recent vapor deposition studies [31]. We find a dramatic depletion of active TLS (those with a tunnel splitting \( \sim 1 \) K) as a function of decreasing quench rate, just as found in recent experiments [32–37]. Use of a state-of-the-art reaction path-finding protocol [38, 39] allows us to efficiently locate double-well potentials in the

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as the energy levels $E_i$ of tunneling centers. The effective density of tunneling states with sufficient statistics to avoid any kind of extrapolation. This sampling enables the determination of the degree of localization associated with individual TLS, and hence provides a detailed, real-space understanding of how atoms participate in tunneling motion and how the thermal exploration of the energy landscape in well-annealed amorphous materials determines the effective density of tunneling centers.

Glass preparation – Past work on the local landscape of low temperature glasses has focused on simple models for real systems such as NiP [24] and silica [29, 30]. Here we study a polydisperse mixture of particles interacting through an inverse power law potential [31]. Our choice is motivated by the fact that the low-temperature behavior of glasses is apparently universal, and should not depend on the particular form of the interactions between atoms or molecules. Given the vast palette of existing glass-forming models, our particular model was chosen in order to enable the thermalization of the system on the computer in a manner that makes direct connection to laboratory experiments. We thus choose a system for which swap Monte Carlo is maximally efficient [31].

We provide minimal details on the system and measures of equilibration in the main text; additional information may be found in the Appendix. We simulate a non-additive polydisperse mixture of $N = 1500$ particles of mass $m_0$. Two particles $i$ and $j$ separated by a distance $r_{ij}$ interact via the potential

$$v(r_{ij}) = \epsilon \left( \frac{\sigma_{ij}}{r_{ij}} \right)^\alpha + \epsilon F(r_{ij}/\sigma_{ij})$$

only if $r_{ij} < r_{cut} = 1.25\sigma_{ij}$, $\sigma_{ij}$ being the non-additive interaction length scale. The function $F$ is a fourth-order polynomial which guarantees the continuity of the potential up to the second derivative at $r_{cut}$. We characterize the physical classical dynamics of the model using molecular dynamics (MD) with energies and lengths expressed in units of $\epsilon$ and the average diameter $\sigma$, respectively. Times measured during MD simulations are expressed in units of $\sqrt{\epsilon/m_0\sigma^2}$. In these units, the number density is $\rho = 1$. The relaxation time $\tau_o$ of the equilibrium fluid is measured from the self-intermediate scattering function $F_s(k = 7.0, \tau_o) = e^{-1}$. The onset of glassy dynamics, signaled by deviations from Arrhenius behavior of $\tau_{\alpha}$, takes place at $T_o = 0.18$, where $\tau_{\alpha}(T_o) = \tau_o$, while the mode-coupling crossover temperature is located at $T_{MCT} = 0.104$ [31].

We analyze in silico glasses by preparing fully equilibrated configurations, using the swap Monte Carlo algorithm, at various preparation temperatures $T_f$, which are then rapidly cooled to lower temperatures using regular molecular dynamics. Therefore, $T_f$ represents the “temperature at which the glass would find itself in equilibrium if suddenly brought to it from its given state,” which is precisely the definition of a “fictive temperature” given by Tool [40]. The temperature $T_f$ characterizes the degree of stability of the computer glasses, see Fig. 1(a). In experiments, $T_f$ would be determined by the cooling rate [41, 42], or by the substrate temperature in a vapor deposition experiment [43–46]. To maximise the analysed range of glass stabilities, we present results for poorly annealed (or, hyperquenched) glasses ($T_f = 0.092$, slightly below $T_{MCT}$) with $\log(\tau_{\alpha}/\tau_o) = 4.9$, liquid-cooled experimental glasses ($T_f = 0.07 \simeq T_g$, with $\log(\tau_{\alpha}/\tau_o) = 10.7$), and ultrastable vapor-deposited glasses ($T_f = 0.062$, with $\log(\tau_{\alpha}/\tau_o) = 14.8$). To obtain statistically significant results, we analyze $N_g$ independent samples ($N_g = 200, 50, 15$ for increasing $T_f$).

Landscape exploration – Our goal is to identify transitions between nearby minima, or double well potentials (DWP) of the potential energy landscape (PEL) of our

FIG. 1. (a) Glasses are prepared at equilibrium (black line) at temperatures $T_f = 0.092, 0.07, 0.062$ (bullets), ranging from hyperquenched to ultrastable. Their potential energy is followed after rapid temperature changes (colored lines). (b) One-dimensional sketch of the potential energy landscape. Molecular dynamics simulations performed at $T_{MD} = 0.04$ are employed to detect double-well potentials (blue). (c) Zoom of one double well potential $V(\xi)$ detected in a glass prepared at $T_f = 0.082$. The classical asymmetry $\Delta E$, activation energy $V_a$, and energy barrier $V = V_a - \Delta E/2$ are illustrated, as well as the energy levels $E_1$ and $E_2$ of the ground state doublet, obtained by solving the 1d Schrödinger equation.

multi-dimensional potential energy landscape, yielding a direct sampling of active tunneling states with sufficient statistics to avoid any kind of extrapolation. This sampling enables the determination of the degree of localization associated with individual TLS, and hence provides a detailed, real-space understanding of how atoms participate in tunneling motion and how the thermal exploration of the energy landscape in well-annealed amorphous materials determines the effective density of tunneling centers.
glassy configurations. Detailed information may be found in the Appendix. Briefly, starting from the configurations equilibrated at $T_f$, we run MD simulations at a temperature $T_{MD} = 0.04$, which is sufficiently low to confine each glass in a single metabasin but is high enough that the system can easily visit many distinct minima (or, inherent structures) within the metabasin [23], see Fig. 1(b).

By repeatedly sampling inherent structures during MD trajectories, we obtain a library of visited local minima. We then identify pairs of minima that are dynamically connected. For each of the $N_g$ starting configurations, we use the isoconfigurational ensemble [47], and run up to 200 simulations starting from the same initial configuration with randomly assigned velocities. The number of isoconfigurational runs, as well as their duration, needs to be large enough for the probability distributions of the inherent structures potential energy $P(E_i)$, and the number of transitions $P(T_{ij})$, to converge to stationary results. While we reach convergence of the probability distributions, we do not sample all potential energy minima and transitions, and their absolute numbers keep increasing with time. We however obtain a significant amount of them, namely 13252, 26898, 848698 minima for $T_f = 0.062, 0.07, 0.092$, respectively. As shown below, these numbers are large enough to directly determine the density of tunneling TLS, which is our main goal.

We select transitions between adjacent minima as described in the Appendix, for which we compute the minimum energy paths connecting them using a climbing image Nudged Elastic Band (NEB) algorithm [38, 39], which ensures that one of the images lies at the saddle point and provides a smooth potential energy profile. In most cases, double wells are obtained. Occasionally, especially for $T_f = 0.092$, the energy profile contains intermediate minima. In such cases, we apply an iterative method to split multiple wells into distinct DWPs, which are then analyzed similarly to the other ones.

We parametrize the minimum energy path of a DWP by $\xi$ such that $\xi = 0$ and $\xi = 1$ correspond to the locations of the two minima (we arbitrarily choose $\xi = 0$ for the deepest minimum), see Fig. 1(c). A DWP is characterized by its asymmetry $\Delta E = V(1) - V(0)$, its energy barrier $V = V_s - \Delta E/2$, where $V_s$ is the activation energy, and by the distance $d$ between minima. The distance is calculated along the reaction coordinate given by the NEB, as the sum of Euclidean distances between images of the system: $d^2 = \sum_{i,\mu} d_{i,\mu}^2$, where $d_{i,\mu}$ is the displacement of particle $i$ in direction $\mu = x, y, z$. The number of particles participating in the transition is characterized by the participation ratio, defined as $PR = (\sum_{i,\mu} d_{i,\mu}^2)^2/(\sum_{i,\mu} d_{i,\mu}^4)$.

The statistics of the classical DWP parameters are shown in Fig. 2. The probability distribution function (pdf) for each quantity is given for different preparation temperatures $T_f$. The pdfs for $T_f = 0.062$ and $0.07$ agree quantitatively, within noise, while we observe an evolution of the pdfs from $T_f \leq 0.07$ to $T_f = 0.092$. In particular, the pdfs of asymmetries and energy barriers are almost exponential in all glasses. The mild dependence of these tails may stem from the fact that the sampling temperature $T_{MD}$ sets a limit on the DWPs that can be detected, independently of $T_f$ (see Appendix for the effect of $T_{MD}$). The pdfs of distances (not shown) and participation ratios vary more significantly between $T_f \leq 0.07$ and $T_f = 0.092$. Since $d \propto \sqrt{PR}$, an increase of $PR$ will affect the distribution of $d$. To eliminate this effect we present the pdf of $d/\sqrt{PR}$ instead of $d$. This quantity can be interpreted as an average displacement of the particles that participate in the transition. On average, the number of particles involved in DWPs is larger in poorly
annealed glasses, while the displacements of individual particles remain comparable. To our knowledge, a dependence on the quench rate of the classical parameters of DWPs has not been reported before.

Density of two-level systems – At sufficiently low temperatures, thermal activation over the energy barrier $V$ is suppressed, but quantum tunneling becomes important [48]. For all subsequent analysis, we reduce our problem to a one dimensional (1d) effective Schrödinger equation along the reaction coordinate. Following Vineyard [49], the effective mass remains $m_0$, with a reaction coordinate $x \in [0, d]$. Using the normalized variable $\xi = x/d$, and scaling energies by $\epsilon$, we obtain

$$ -\frac{\hbar^2}{2m_0d^2\epsilon} \partial_x^2 \Psi(\xi) + V(\xi) \Psi(\xi) = E\Psi(\xi), \quad (2) $$

where the “quantumness” of the problem is controlled by the adimensional mass $\tilde{m}_0 = m_0\sigma^2/\hbar^2$ (see Fig. 3). In general, the Laplacian should take into account curvature effects, which are neglected here for simplicity. Additionally, the potential $V(\xi)$ obtained from the NEB is defined only for $\xi \in [0, 1]$. An extrapolation outside this interval is needed to solve Eq. (2), see the Appendix.

We solve Eq. (2) for all DWPs analyzed in Fig. 2. In particular, we compute the first two energy levels of the double well, $E_1$ and $E_2$, and define the tunnel splitting $\delta E = E_2 - E_1$. As an illustration, we show in Fig. 1(c) the two energy levels and the tunnel splitting of a DWP. The tunnel splitting $\delta E$ is the relevant parameter when it comes to low-temperature properties. When $T$ is low, the transitions that occur by quantum tunneling have a tunnel splitting $\delta E \sim T$ [6]. These particular DWPs are called tunneling two-level systems (TLS).

We characterize the distribution of TLS using a cumulative distribution of tunnel splittings $n(\delta E)$, defined as the number of DWPs with tunnel splitting smaller than $\delta E$, normalized by the number of particles $N$ in the glass, and the number of independent analyzed samples $N_g$. In TLS theory, $n(\delta E)$ can be expanded as $n(\delta E) \approx n_0 \delta E + O(\delta E^2)$ for small tunnel splittings, and the specific heat at low temperature is linear with $T$, with $n_0$ entering the prefactor [3, 6].

In order to estimate the density $n_0$ of TLS and to analyze its dependence on glass stability, we plot $n(\delta E)/\delta E$ as a function of tunnel splitting in Fig. 3. The curves have a similar shape, indicating a saturation to a plateau value, $n_0$, at low tunnel splittings. The existence of a plateau in these curves demonstrates that we can directly estimate the density of TLS $n_0$ without any extrapolation or uncontrolled hypothesis. The key physical result is that the TLS density $n_0$ (as estimated for example by the values of the curves for $\delta E$ in the range $10^{-3} - 10^{-4}$) decreases by two orders of magnitude when exploring glasses from the hyperquenched to the ultrastable regime. We find almost no TLS with splitting $\delta E < 10^{-4}$ in the most stable glasses. To our knowledge, this constitutes the first numerical evidence for a significant suppression of TLS with increasing glass stability.

Microscopic nature of TLS – How many particles are involved in the tunneling motion of a TLS? [28–30] To establish an accurate picture, we analyzed how the participation ratio $PR$ of transitions correlates with the tunnel splitting $\delta E$. We focus on the low-temperature active TLS with tunnel splittings $\delta E \sim 10^{-3} - 10^{-4}$, and find that the participation ratio can vary from 1 to 200 (see the Appendix). Higher participation ratios ($PR \sim 200$) are found for hyperquenched glasses, while the most collective TLS found in ultrastable glasses have $PR \sim 30$.

Our study thus provides a systematic numerical evidence that TLS are typically very localized, but active TLS are occasionally associated with collective excitations. We provide two snapshots in Fig. 4, corresponding to a collective TLS (left) and a very localized TLS (right) identified in a hyperquenched glass.

Discussion – To relate our data to experiments we must convert our simulation units into physical units. The temperature scale below which quantum effects become important is obtained by comparing the thermal wavelength to the interparticle distance: $T_Q = \frac{2\hbar^2}{m\sigma^2k_B}$. We thus consider DWPs with $\delta E < k_BT_Q$ as low-temperature active TLS, and their total number for $N$ particles and $N_g$ glass samples is $n_{\text{active}} = NN_g n(\delta E = k_BT_Q)$.

A detailed analysis for experimental comparisons may be found in the Appendix. Let us first consider Argon parameters: $\sigma = 3.4 \times 10^{-10}$m, $\epsilon/41 = 1.65 \times 10^{-21}$J, $m_0 = 6 \times 10^{-26}$kg [50]. This gives $T_g \sim 32$K, $T_Q \sim 0.73$K, and $\tilde{m}_0 \sim 4000$. For this value of $\tilde{m}_0$, our values of $n_0$ can be estimated from Fig. 3, within statistical noise, as $n_0^{\text{exp}} \sim 0.4, 0.04$ for $T_f=0.092, 0.07, 0.062$, which gives $n_0^{\text{exp}} \sim 10^{49}, 10^{48}, 10^{47} \text{J}^{-1} \text{m}^{-3}$. Active TLS have $\delta E < k_BT_Q = 0.0015\epsilon$ and we find $n_{\text{active}} = 1000,$

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4.png}
\caption{Snapshots of TLS with low tunnel splitting $\delta E$ for $T_f = 0.092$ and $\tilde{m}_0 = 30000$. (a) $PR \approx 126$ with $\delta E = 8.9 \times 10^{-5}$. (b) $PR \approx 1.6$ and similarly low $\delta E = 5.4 \times 10^{-5}$. The size and color of particles are proportional to their displacement between the initial and final configurations of the TLS, normalized to the highest displacement.}
\end{figure}
291, 61 such TLS for $T_g = 0.092, 0.07, 0.062$ respectively. A second choice would be to use Nickel as a reference material as motivated by NiP metallic glasses [24], where $\sigma = 2.21 \times 10^{-10} \text{m}, \epsilon = 6.14 \times 10^{-20} \text{J}, n_0 = 1.02 \times 10^{-28} \text{kg}$ [51]. In this case, we have $T_g \sim 298 \text{K}, T_D \sim 0.9 \text{K}$, and $\bar{m}_0 \sim 30000$. For this value of $\bar{m}_0$, from Fig. 3 we find $n_0^{\text{sim}} \sim 60, 6, 0.6$ for $T_f = 0.092, 0.07, 0.062$, which gives $n_0^{\text{exp}} \sim 10^{30}, 10^{49}, 10^{48} \text{J}^{-1} \text{m}^{-3}$. Active TLS have $\delta E < k_B T_Q \sim 0.0002c$ and we find $n_{\text{active}} = 248, 46, 28$ such TLS for $T_g = 0.092, 0.07, 0.062$ respectively.

Experimentally, a typical value of $n_0 \sim 10^{46} \text{J}^{-1} \text{m}^{-3}$ is reported [6, 7]. Our corresponding estimate for $T_f = 0.07$ is larger by a factor of $\sim 10^2$ for Argon and $\sim 10^3$ for Nickel. This discrepancy may be explained by the fact that we include in our estimates all DWPs detected at temperature $T_{\text{MD}} = 0.04 \gg T_Q$, while in the real experiment the glass is brought directly to $T_Q$ and only a small fraction of DWPs that lie at the very bottom of the energy metabasin is observed. In fact, it is well known that $n_0 \sim \log(\tau)$ where $\tau$ is the observation time at $T_Q$ [6]. This behavior should exist up to a natural cutoff corresponding to the timescale of complete exploration of the energy landscape. Our exploration protocol at $T_{\text{MD}} \gg T_Q$ should then correspond to artificially setting the value of $\tau$ close to this natural cutoff.

Despite this, the reduction of $n_0$ by two orders of magnitude when moving from hyperquenched to ultrastable glasses is very robust and in very good agreement with recent experimental results [34, 37]. Our results also demonstrate that glass ultrastability (rather than the vapor-deposition process) is responsible for the depletion of TLS. Finally, our detailed analysis of tunneling TLS in a simple computer model demonstrates their importance to understand low-temperature glass anomalies, in particular the linear temperature dependence of the specific heat (see Appendix). While several recent works advocated the idea that quantized non-trivial low-frequency modes alone could explain this behavior [10, 18, 52–56], our numerics instead suggests that the specific heat of structural glasses is dominated by tunneling TLS, as originally proposed in [3, 6].

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Appendix A: Model

We study a three-dimensional, non-additive, continuously polydisperse mixture of particles interacting via the pair potential Eq. (1). The particle diameters $\sigma_i$ are drawn from the normalized distribution $P(0.73 < \sigma < 1.62) \sim 1/\sigma^3$, with average diameter $\langle \sigma \rangle = \int P(\sigma)d\sigma = 1$ (simply denoted as $\sigma$ in the main text). We employ a non-additive cross-diameter $\sigma_{ij} = 0.5(\sigma_i + \sigma_j)(1 - 0.2|\sigma_i - \sigma_j|)$. This model is efficiently simulated with the swap Monte Carlo algorithm. The choice of particle dispersity and non-additivity make the homogeneous fluid robust against fractionation and crystallization at all temperatures numerically explorable [31]. As in the main text, classical quantities are given in units of $\epsilon, \sigma, m_0$.

We characterize the dynamic slowdown of the supercooled liquid using molecular dynamics (MD) simulations. The temperature evolution of the relaxation time $\tau_\alpha$ provides three temperatures relevant to this work. The onset of glassy dynamics, signaled by deviations from Arrhenius behavior, takes place at $T_o = 0.18$, where $\tau_\alpha(T_o) = \tau_o$. The mode-coupling crossover temperature $T_{MCT} = 0.104$ is measured by fitting the relaxation time data to $\tau_\alpha \sim (T - T_{MCT})^{-\gamma}$ in a limited window of relatively high temperatures. At $T_{MCT}$, the dynamics is four orders of magnitude slower than at the onset temperature, $\tau_\alpha(T_{MCT}) \simeq 10^4 \tau_o$. We take the mode-coupling crossover temperature $T_{MCT}$ as a proxy for the computer glass transition, below which standard MD fail to equilibrate the homogeneous fluid. The experimental glass transition $T_g = 0.067$ is located by fitting the relaxation time data to a parabolic law, using $\tau_\alpha(T_g) = 10^{12}\tau_o$ [31].

This glass-forming model is efficiently simulated at equilibrium with the swap Monte Carlo algorithm. Supercooled liquid configurations can be generated down to $T = 0.062$, i.e. below the experimental glass transition $T_g$. In this work, we focus on configurations prepared in equilibrium conditions at temperatures $T_f = 0.092, 0.07, 0.062$. For the two lowest $T_f$ values, standard MD dynamics initialized from an equilibrium configuration is completely arrested: no diffusion is observed and the system is trapped within a glass metabasin. For the higher $T_f = 0.092$, some diffusion is observed in equilibrium; but if the system is rapidly cooled at lower temperatures, once again no diffusion is observed and a glass state is obtained. Borrowing from experimental conventions [40], we call this the “fictive temperature” of the glasses, as discussed in the main text.

Appendix B: Landscape exploration

The amorphous configurations generated at $T_f$ are first thermalized to $T_{MD} = 0.04$ using a Berendsen thermostat. At this temperature, no diffusion is observed for all glasses. The system is then simulated in the NVE ensemble, using an integration time step of $dt = 0.01$. Configurations along the MD trajectory are frequently minimized using a conjugate gradient algorithm, bringing them to their inherent structure (IS), i.e. the nearest local minimum in the potential energy landscape (PEL). We minimize the MD trajectory every 20, 10, 5 time steps for $T_f = 0.062, 0.07, 0.092$. The high frequency of minimization is chosen to identify nearby local minima, separated by an energy barrier.

From the MD simulations, we obtain a time series of inherent structures. We are interested in transitions between two different inherent structures, identified by comparing two consecutive minima. We recorded 70970, 130859, and 159359 transitions between inherent structures, for $T_f = 0.062, 0.07, 0.092$ respectively. We wish to characterize the potential energy barriers corresponding to the transitions. This analysis is computationally costly. Given the large number of transitions detected, we chose to analyze transitions detected at least 4 times, regardless of the direction of the transition ($A \to B$, or $B \to A$). The number of transitions analyzed is equal to 14195, 23535, and 117361, for $T_f = 0.062, 0.07, 0.092$ respectively.

In order to investigate the influence of the temperature $T_{MD}$ on the characteristics of the double well potentials identified, we present in Fig. S1 the probability distribution function of potential energy barriers identified with $T_{MD} = 0.01$, and 0.04 (used in the main text). The sampling temperature $T_{MD}$ influences the tail of the distribution only, which decays as $\exp(-V/T_{MD})$. We conclude that the sampling of relevant TLS is not affected by a variation of $T_{MD}$ within a reasonable interval.
Appendix C: Tunnel splitting

For each analyzed transition, the Nudged Elastic Band (NEB) algorithm outputs a one-dimensional potential defined for the reduced coordinate $\xi$, between the two minima only. We run the algorithm using 40 images of the system. We need to extrapolate the potential in order to obtain a full double well potential. We tested various extrapolation schemes, such as parabolic fitting of the minima, and mirroring around each minima, defining $V(-\xi) = V(\xi)$ for $\xi < \xi_a$ and $V(2-\xi) = V(\xi)$ for $\xi > \xi_a$, where $\xi_a$ is the coordinate of the potential maximum: $V(\xi_a) = V(0) + V_a$. In the main text, we used a linear extrapolation of the reaction path obtained with the NEB. Let us denote $r_1$ and $r_2$ the coordinates of the particles in the first two images of the system along the reaction path ($r_1$ is an energy minimum). We measure the potential energy of the configuration, starting from $r_1$, and moving in the direction $r_1 - r_2$. We perform a similar extrapolation at the other minimum. We show in Fig. 1 a double-well potential obtained from the NEB algorithm (blue part), and by linear extrapolation of the reaction path (black part). We have compared all methods and found that while each scheme gives a slightly different potential, the statistics of tunnel splittings remains unaffected by our choice. In the main text, we use the most physical scheme, namely the linear extrapolation of the reaction path.

Once the classical potential $V(\xi)$ is obtained by extrapolation as discussed above, we solve numerically the Schrödinger Eq. (2) using a standard Python package. Note that, in general, the Laplacian term should take into account curvature effects along the reaction coordinate, $\nabla^2 \xi = \partial^2 \xi + \frac{(\text{det} g)^{-1/2}}{\partial \xi_i}[(\text{det} g)^{1/2} \partial_i] - \frac{(\text{det} g)^{-1/2}}{\partial \xi_i}[(\text{det} g)^{1/2} \partial_i]$, where $g$ is a metric tensor and $\xi_i$ are coordinates orthogonal to $\xi$. For simplicity, we neglect these effects and use the standard second derivative along the reaction coordinate.

We present in Fig. S2 a scatter plot of the tunnel splitting $\delta E$ as a function of participation ratio $PR$ and energy barrier $V$ for DWPs identified in glasses from hyper-quenched (top) to ultrastable (bottom). In Fig. S2 (a,c,e) we observe that in the relevant range of $\delta E \lesssim 10^{-3}$ the value of $PR$ can be as large as $\sim 200$ for $T_f = 0.092$ and $\sim 30$ for $T_f = 0.062$. In Fig. S2 (b,d,f) we observe that in the same relevant range, the barrier is always $V \gtrsim 10^{-2} \gg \delta E$, indicating that the relevant DWP are indeed TLS. We also checked (not shown) that in the same range, one always has $E_3 - E_1 \gg \delta E$, where $E_3$ is the third energy level. Finally, we checked that for most TLS in the relevant range, the wavefunctions of the first two levels are delocalized over the two wells; for a fraction of them, however, the wavefunctions are localized, indicating that tunnelling is suppressed. These TLS would be frozen in experimental conditions, which also provides an additional explanation for why our simulations overestimate $n_0$ with respect to experiments.

Appendix D: Dimensional scaling analysis for unit conversion

The number of TLS per particle in a given glass sample with a tunnel splitting less than $\delta E$, for $\delta E \to 0$, is $n_0 \delta E$. Hence, $n_0$ has the dimensions of an inverse energy, expressed in units of $e^{-1}$. However, because in our simulation
FIG. S2. Scatter plot of the participation ratio $PR$ (a,c,e) and the potential energy barrier $V$ (b,d,f) versus the tunnel splitting $\delta E$, of double-well potentials in glasses prepared at $T_f = 0.092$ (a-b), $T_f = 0.07$ (c-d), and $T_f = 0.062$ (e-f). The data for DWPs found in the same glass sample (there are $N_g$ of them) are presented with the same color. The tunnel splittings are computed using an adimensional mass $\tilde{m}_0 = 30000$.

units the number density is $\rho = 1$, $n_0$ is also the number of TLS per unit volume, in units of $\epsilon^{-1}\sigma^{-3}$, i.e.

$$n_0^{\text{exp}} = n_0^{\text{sim}} \times \epsilon^{-1}\sigma^{-3}. \quad (D1)$$

For Argon, $\epsilon^{-1}\sigma^{-3} \sim 3.85 \times 10^{48} \text{J}^{-1} \text{m}^{-3}$, while for Nickel $\epsilon^{-1}\sigma^{-3} \sim 1.51 \times 10^{48} \text{J}^{-1} \text{m}^{-3}$, which allows one to convert our numerical results for $n_0^{\text{sim}}$ into experimental values for these two materials.

Because the glass transition temperature in the simulation is $T_g = 0.067$, the corresponding glass transition temperature in physical units is

$$T_g = 0.067 \times \epsilon \frac{k_B}{\sigma}. \quad (D2)$$

Finally, the temperature $T_Q$ at which quantum effects become relevant is that at which the thermal wavelength equals the interparticle distance. Since our simulation density is $\rho = 1/\sigma^3$, we get

$$T_Q = \frac{2\pi \hbar^2}{m_0 \sigma^2 k_B} = \frac{2\pi \epsilon}{\tilde{m}_0 \hbar k_B}, \quad (D3)$$

and we recall that $\tilde{m}_0 = m_0 \sigma^2 \epsilon / \hbar^2$ is the adimensional mass that appears in the Schrödinger equation. Finally, note
that the relevant (active) TLS are those with \( \delta E < k_B T_Q \), and their total number in our simulation is given by

\[
n_{\text{active}} = NN_g n (\delta E = k_B T_Q) \\
\sim NN_g n_0^{\text{sim}} \frac{k_B T Q}{\epsilon} = 2\pi NN_g n_0^{\text{sim}} \frac{n_0}{m_0}. \tag{D4}
\]

We find that \( n_0/\tilde{m}_0 \) is roughly constant for a given glass stability \( T_f \), as shown in Fig. S3. This results implies that the choice of \( \tilde{m}_0 \) can be quite arbitrary, within a reasonable range. In particular, \( \tilde{m}_0 \) cannot be too small otherwise the condition \( T_Q \ll T_g \) would be violated.

**Appendix E: Vibrational and TLS contributions to the specific heat**

Here, we compare the contributions to specific heat coming from TLS and from harmonic vibrations around an inherent structure. To obtain the TLS contribution, for a given \( T_f \) and \( \tilde{m}_0 \), we collect all the TLS found in all the \( N_g \) glasses, with splitting \( \delta E_i \), and compute \[3, 6\]

\[
C_{\text{TLS}} = \frac{1}{N N_g} \sum_i \frac{x_i^2 \cosh(x_i)^2}{\cosh(x_i)^2}, \quad x_i = \frac{\delta E_i}{2 k_B T}. \tag{E1}
\]

To obtain the vibrational contribution, we considered a single glass prepared at \( T_f = 0.062 \), and all the \( N_{\text{IS}} \) inherent structures found within that glass. For each inherent structure, we diagonalize the Hessian matrix of the classical potential, to obtain a set of eigenvalues (spring constants) \( \kappa_\alpha \). Each of these provides a quantum harmonic oscillator contribution to the vibrational specific heat, which is

\[
C_{\text{vib}} = \frac{1}{N N_{\text{IS}}} \sum_\alpha \frac{x_\alpha^2}{\sinh(x_\alpha)^2}, \quad x_\alpha = \frac{\hbar \omega_\alpha}{2 k_B T}, \quad \omega_\alpha = \sqrt{\frac{\kappa_\alpha}{m_0}}. \tag{E2}
\]

Note that the finite size of the system imposes a cutoff on the low-frequency Debye behavior. In fact, the lowest frequency found in our system is \( \hbar \omega_\alpha/k_B = 0.0038 \) (in simulation units) for \( \tilde{m}_0 = 5000 \), and \( \hbar \omega_\alpha/k_B = 0.0016 \) for \( \tilde{m}_0 = 30000 \). Hence, for \( T \lesssim 10^{-3} \) the Debye behavior is cutoff and an exponential (Einstein) behavior is observed.

Yet, from Fig. S4 we conclude that the vibrational contribution decays much faster than the TLS one upon lowering temperature, and that already at \( T \sim 10^{-4} \) we have \( C_{\text{vib}} \ll C_{\text{TLS}} \) for all considered values of \( \tilde{m}_0 \) and \( T_f \).
FIG. S4. (a) TLS contribution to the specific heat per particle, as a function of $T$. Dotted-dashed lines are the asymptotic low-temperature scaling, $C_{\text{TLS}} \sim T$, for $\tilde{m}_0 = 30000$ (for $\tilde{m}_0 = 5000$ the statistics is not sufficient for a good extrapolation). (b) Vibrational contribution to the specific heat per particle, as a function of $T$, for $T_f = 0.062$, averaged over inherent structures in a typical glass metabasin. The $T^3$ behaviour is cutoff at low $T$ due to finite size effects.