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History dependence of a two-level system

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Glasses have history dependence because they are not in equilibrium. A quantitative understanding of the history dependence of glasses cannot be achieved until we have a quantitative theory of the glass state and the equilibrium glass critical point. But we can still rely on some simple glasslike models to gain some qualitative understanding about them. In this paper, we study the history dependence of a two-level-system model by calculating the linear response of its physical properties to small variations in the thermal history. We calculate the linear response of the mean energy to changes in the temperature—the nonequilibrium analogs of the specific heat. We calculate the linear response of the mean thermodynamic entropy exactly, and the linear response of the entropy probability distribution using matched asymptotic expansions.

Glasses are not in equilibrium. Therefore, their properties depend on their thermal history. For example, if we cool a glass and then heat it back, the specific heat of the glass measured during heating will be different from the specific heat measured during cooling,[1] having an extra bump near the glass transition. As another example, the density of a glass is larger if the glass is cooled more slowly from a melt.[2] Also, the low-temperature glass properties are dominated by the localized two-level-system tunneling centers[3,4] whose number at low temperatures (say, in vitreous silica) increase as the glass is formed through faster cooling.[5] A full quantitative understanding of these properties could be technically important; one might use it to make glasses with desired qualities by tuning their thermal history. Unfortunately, until we have a quantitative theory of the nature of glass state and the equilibrium glass critical point, it will not be possible to calculate quantitatively the history dependence of a glass. Nonetheless, by studying simple models that have glasslike behaviors, we hope to gain some qualitative understanding of history dependence in glasses. This is the main object of this paper.

Since we do not have an equilibrium theory of real glasses to work from, we will rely on some simple models to understand the qualitative properties of glass history dependence. In this paper we choose a thermally activated two-level system (TLS) as our simple model for high-temperature glassy dynamic properties. This model has been previously studied by Bar-Yam, Adler, and Joannopoulos[6] and was used by Langer *et al.*[7–9] to understand the low-temperature glass entropy distributions. (See also Brey and Prados.[10]) Although it is a very simple model, a TLS is glasslike[8] and in particular has history dependence.

In Refs. 7–9, among other things, Langer *et al.* used matched asymptotic expansions to compute the energy and thermal entropy distribution of a TLS in the limit of slow cooling for a special smooth cooling schedule. For history dependence, by numerical simulation, they have studied the effect of quenching in the thermal history on a TLS and a small-spin-glass-lattice low-temperature residue entropy distribution. In this paper we will systematically study the history dependence of a TLS. We will calculate the thermal history dependence of the TLS low-temperature average energy and thermal entropy. Using asymptotic expansions, we will calculate the thermal history dependence of the TLS low-temperature entropy distributions and analytically understand the physics of the numerical simulation results of TLS with quenched thermal history as obtained by Langer, Sethna, and Grannan.[9] In the process we will redo the asymptotic analysis of the TLS entropy distribution for the special smooth cooling schedule and correct some mistakes in the earlier analysis.

The history dependence of a glass can be described mathematically through linear response. In thermodynamics the equilibrium "magnetic-field dependence of a system" is described by the linear response of various physical quantities of the system with respect to an external magnetic field. In particular, the linear response of the magnetization with respect to the external magnetic field is just the magnetic susceptibility $\chi = dM/dH$. In the same way we can best describe the thermal history dependence of nonequilibrium glass through the linear response of its physical properties with respect to small perturbations of the glass thermal history.

The usefulness of these glassy response functions depends on the range of validity of linear response. If small changes in the cooling schedule made large changes in the density, linear response probably would not be useful. On the contrary, the value, for example, of the fictive temperature changes very little for a relatively large change of cooling rate.[11] One expects that the linear-response regime may extend throughout the available experimental range. In our calculation of the TLS history dependence, we will use linear-response formulations.

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In this paper we will introduce a TLS model, and calculate the average energy and thermal entropy for arbitrary cooling schedules exactly. We then study the history dependence of the average energy and entropy through linear response around a chosen smooth cooling schedule. Finally, we will briefly discuss the history dependence of the entropy distribution, leaving the details of the analysis in Appendixes A–C.

A TLS (shown in Fig. 1) can be in one of two states, with energy 0 (for the lower state) and ϵ (for the upper state). A barrier of height V (from the upper state) exists for transitions between the two states. Transitions take place by thermal excitations over the barrier with a rate given by

$$\Gamma_{\uparrow,\downarrow}(T)=\Gamma_0 e^{-\beta V}, \tag{1}$$

for transitions from upper to lower state ($\beta\equiv 1/T$), and

$$\Gamma_{\downarrow,\uparrow}(T)=\Gamma_0 e^{-\beta(V+\epsilon)}, \tag{2}$$

for transitions from lower to upper state. The master equation for the average upper-level population is

$$\frac{dn}{dt}=-\Gamma_{\uparrow,\downarrow}(T)n+\Gamma_{\downarrow,\uparrow}(T)(1-n), \tag{3}$$

with the boundary condition

$$n(T=\infty)=\tfrac{1}{2}. \tag{4}$$

Figure 1 shows a potential energy surface which the reader should envision while thinking about a two-level system. One imagines that only one quantum state in each well is important at low temperatures, but that transitions from one well to the other must be thermally activated over the central barrier.

Let us suppose that an ensemble of identical TLS's (same V and ϵ) are in contact with a heat bath that determines the temperature schedule $T(t)$. Qualitatively, as discussed in Ref. 8, at high temperatures the transition rate $\Gamma_{\uparrow,\downarrow}(T)$ is much larger than the rate of change of the equilibrium upper-level population

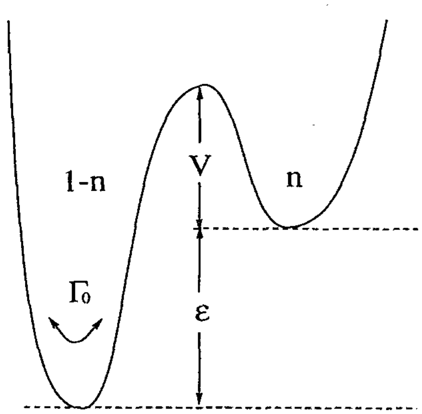

FIG. 1. Two-level system, with barrier height V and asymmetry ϵ. (For the one shown here, the ratio $\mu=\epsilon/V=1.3$.) n is the ensemble average population of the upper well. Γ_0 is the oscillation frequency in the bottom of the wells.

$$n_{\mathrm{eq}}(T)=\frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}. \tag{5}$$

The TLS's then remain nearly in equilibrium. As the temperature is lowered, the TLS's go out of equilibrium at around the "freezing" temperature T^* when the rate of transitions over the barrier is comparable to the cooling rate:

$$\left|\frac{dn_{\mathrm{eq}}}{dt}\right|_{T=T^*}\sim\Gamma_{\uparrow,\downarrow}(T^*)n_{\mathrm{eq}}(T^*), \tag{6}$$

and the upper-level population at lower temperatures roughly remains at the population frozen in at T^*. Quantitatively, we can solve the population master equation (3) exactly for arbitrary cooling schedules and study the linear response of the TLS upper-level population under small variations of cooling schedules and asymmetry around a given cooling schedule $T_{\mathrm{sm}}(t)=T_0/(1+Rt)$. (This cooling schedule was used in Refs. 7–9. From now on we will use subscript "sm" to represent this special cooling schedule.)

We first study the history dependence of the upper-level population n or, equivalently, the average energy. We make the change of variables $x=\exp(-\beta V)$, define a dimensionless asymmetry $\mu=\epsilon/V$, and for cooling schedule $T_{\mathrm{sm}}(t)$ define a dimensionless cooling rate $\delta\equiv RV/T_0\Gamma_0$. Then for the given cooling schedule $T_{\mathrm{sm}}(t)$, the upper-level population is obtained by solving Eq. (3):

$$n_{\mathrm{sm}}(x)=\frac{1}{\delta}\int_x^1 dx_1 x_1^{\mu}\exp\left[\frac{1}{\delta}[h(x_1)-h(x)]\right]+\frac{1}{2}\exp\left[-\frac{1}{\delta}h(x)\right], \tag{7}$$

where

$$h(x)\equiv 1-x+\frac{1-x^{1+\mu}}{1+\mu}. \tag{8}$$

For perturbations around this given cooling schedule,

$$\beta(t)=\beta_{\mathrm{sm}}(t)+\delta\beta(t), \tag{9}$$

the history dependence of the TLS upper-level population can be represented by linear response as follows:

$$n(x)=n_{\mathrm{sm}}(x)+\int_x^1 dx_1\frac{d\delta\beta}{dx_1}\mathcal{N}(x_1,x), \tag{10}$$

with

$$\mathcal{N}(x_1,x)=\frac{dn_{\mathrm{sm}}(x_1,\mu(x_1))}{d\beta_1}\exp\left[\frac{1}{\delta}[h(x_1)-h(x)]\right]. \tag{11}$$

The upper-level population linear-response kernel $\mathcal{N}(x_q,x)$ is the response to the quench depicted in Fig. 2, described by

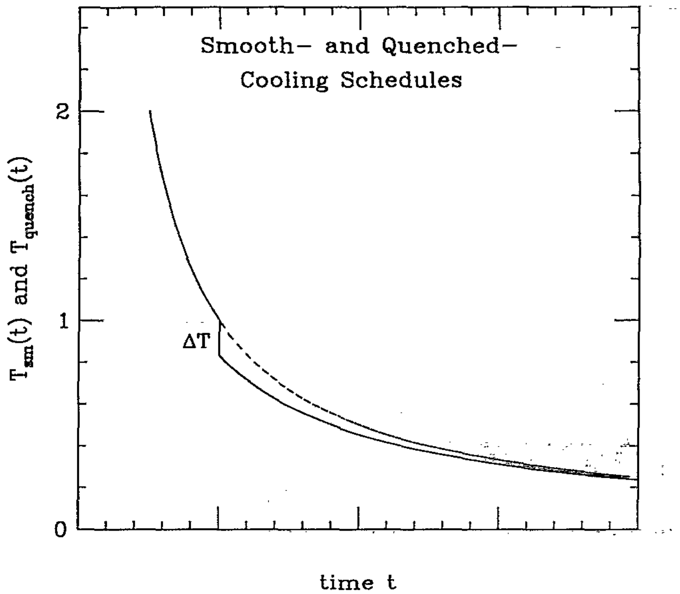

FIG. 2. Chosen smooth cooling schedule (dashed line) and the quenched cooling schedule (solid line). The smooth cooling schedule is described as $\beta_{sm}(t)=\beta_0+rt$ ($\beta_0=0$ here) and the quenched cooling schedule is described in Eq. (12).

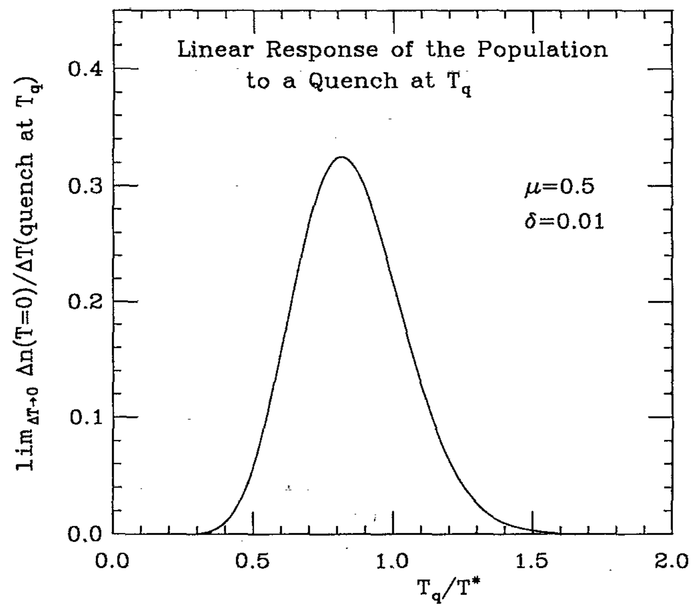

FIG. 3. Linear response of the zero-temperature upper-well population with respect to a small temperature quench at T_q during an otherwise smooth schedule with $\mu=0.5$, $\delta=0.01$. $x(T^*)=\delta$, where T^* is defined as the freezing temperature. The units are set by $V=k_B=1$ from Figs. 3–7 to make all the axis labels dimensionless.

$$\beta(t)=\begin{cases}\beta_0+\dfrac{R}{T_0}t & \text{for } t<t_q=T_0(\beta_q-\beta_0)/R\ ,\\[2ex] \beta_0+\Delta\beta+\dfrac{R}{T_0}t & \text{for } t\geq t_q\ .\end{cases} \tag{12}$$

For a temperature jump ΔT, the change of the upper-level population at temperature $x(T)$ is

$$\lim_{\Delta T\to 0}\frac{\Delta n(x)}{\Delta T}=\frac{d\beta_q}{dT_q}\mathcal{N}(x_q,x)\ . \tag{13}$$

In Fig. 3 we have plotted the zero-temperature population response to a quench at T_q: $(d\beta_q/dT_q)\mathcal{N}(x(T_q),x(T=0))$ for $\mu=0.5$ and $\delta=0.01$. The freezing temperature T^* is defined through $x(T^*)=\delta$. From Fig. 3 we see that the zero-temperature population is only sensitive to temperature quenches around the freezing temperature. The memory of quenches far above the freezing temperature is washed away by the rapid equilibrations due to the large thermal fluctuations, while quenches far below the freezing temperature do not change the zero-temperature population because the TLS degree of freedom is already frozen out. Similarly, we can also study the TLS population history dependence on the TLS asymmetry and barrier height history. We will not include them here. Also, one can get other information[12] from the kernel $\mathcal{N}(x_q,x)$.

The second history dependence property of the TLS that we study is that of the thermodynamic entropy. As discussed by Langer, Dorsey, and Sethna,[8] thermodynamic entropy is defined through heat exchange between the system and the heat bath $\Delta S=\int dQ/T$, unlike the statistical entropy which measures the available volume of phase space. These two kinds of entropy have the same value for an equilibrium system, but differ for nonequilibrium systems; they differ by the irreversible entropy generated on cooling. Since glasses are not in equilibrium, we need to distinguish them. The entropy measured in experiments is the thermodynamic entropy. Because the statistical entropy is given simply in terms of the upper well population n, we will refer with entropy always to the thermodynamic entropy. Here we will calculate the average thermodynamic entropy of a TLS and its thermal history dependence.

The master equation for the average entropy is

$$\frac{d\bar{S}}{dt}=\beta\epsilon[-\Gamma_{\uparrow,\downarrow}(T)n+\Gamma_{\downarrow,\uparrow}(T)(1-n)]\ , \tag{14}$$

with the boundary condition chosen as

$$\bar{S}(T=\infty)=\ln 2\ . \tag{15}$$

We can solve this master equation for average entropy exactly and study the linear response of the average entropy under small variations of the cooling schedules.

For cooling schedule $T_{sm}(t)$, we have,

$$\bar{S}_{sm}(x)=\ln 2+\frac{\mu}{\delta}\int_x^1 dx_1 \ln x_1[(1+x_1^\mu)n_{sm}(x_1)-x_1^\mu]\ , \tag{16}$$

where $n_{sm}(x)$ is determined by Eq. (7). For a small thermal history perturbation described by $\beta(t)=\beta_{sm}(t)+\delta\beta(t)$ around the given smooth cooling schedule $\beta_{sm}(t)$, with linear-response formulation, we have,

$$\bar{S}(x)=\bar{S}_{sm}(x)+\int_x^1 dx_1 \frac{d\delta\beta}{dx_1}\Sigma(x_1,x) , \quad (17)$$

where $\Sigma(x_1,x)$ can be written as

$$\Sigma(x_1,x)=\frac{d\bar{S}_{sm}(x_1)}{d\beta_1}+\frac{dn_{sm}(x_1)}{d\beta_1}\frac{\mu}{\delta} \times \int_x^{x_1} dx_2 \ln x_2 (1+x_2^{\mu}) \times \exp\left[\frac{1}{\delta}[h(x_1)-h(x_2)]\right] . \quad (18)$$

The first term is due to the delay (because of the quench) of the loss of heat caused by transitions from upper to lower level. It effectively increases the zero-temperature entropy. The second term is due to the transitions from upper to lower level of those quench-delayed excess particles in the upper level. This effectively decreases the zero-temperature entropy. The average entropy linear-response kernel $(d\beta_q/dT_q)\Sigma(x_1,x)$ is plotted in Fig. 4 for $\mu=0.5$ and $\delta=0.01$. It represents the linear response of the zero-temperature average entropy due to a small temperature quench at T_q described by Eq. (12) as follows:

$$\lim_{\Delta T\to 0}\frac{\Delta\bar{S}(T=0)}{\Delta T}=\frac{d\beta_q}{dT_q}\Sigma(x_q,x=0) .$$

If the quench occurs at a temperature much higher than T^*, the upper to lower transitions delayed by the quench will still happen, but at lower temperatures, and therefore the zero-temperature entropy is decreased as compared with the case without the quench. If the quench occurs at a temperature lower than T^*, some of the transitions that are delayed due to the quench cannot happen because of the low temperature, and this leads to a higher zero-temperature entropy. The crossover occurs at around the freezing temperature T^*.

The third property we study is the distribution of measured entropies. The average thermodynamic entropy does not give a complete description of TLS entropy. Since each TLS (even with the same V and ϵ and the same thermal history) makes transitions independently, we need to use the entropy distribution $\rho(S,T)$ to describe TLS entropy. The concept of entropy distribution was introduced by Langer *et al.*[8,9] We refer readers to Ref. 8 for a detailed introduction or Appendix A for a brief summary. In Appendix A we also make some necessary improvements of their asymptotic solution.

In Fig. 5 we show the new asymptotic solutions of the zero-temperature TLS entropy distribution for the smooth cooling schedule $T_{sm}(t)$ (solid line). Note the double-peaked structure. Those systems which remain stuck in the upper well at $T=0$ lie in the right-hand peak, which is centered near ϵ/T^*. Also shown is a cooling schedule with a temperature quench from $T_1=2.0T^*$ to $T_2=1.0T^*$ (dashed line). The quenched cooling schedule is of the form (12) with $\Delta\beta$ finite. (The approximate formula for the zero-temperature entropy distribution for the quenched schedule is derived in Appendix C.) Note that the zero-temperature entropy distribution with a temperature quench around the freezing temperature

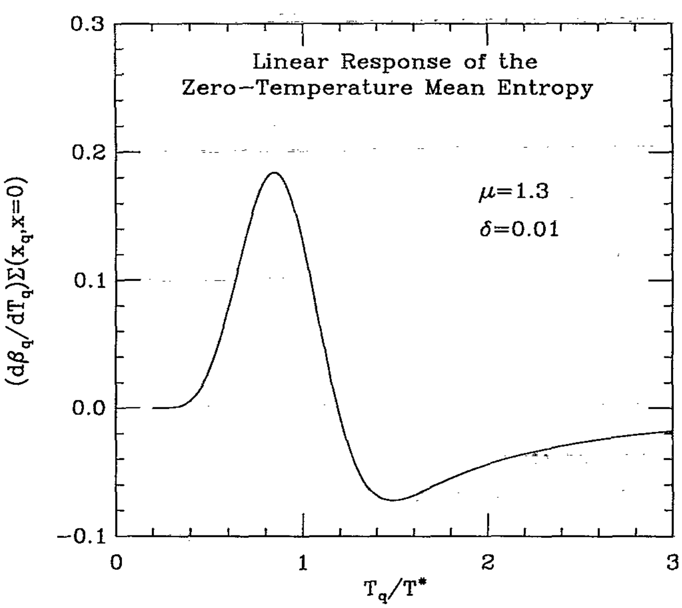

FIG. 4. Linear response of the ensemble-averaged zero-temperature measured thermodynamic entropy with response to a temperature quench at T_q. For high T_q the zero-temperature average entropy decreases because those upper- to lower-level transitions delayed by the quench will still happen, but at lower temperatures. For low T_q the transitions that are delayed cannot happen and lead to a higher zero-temperature entropy.

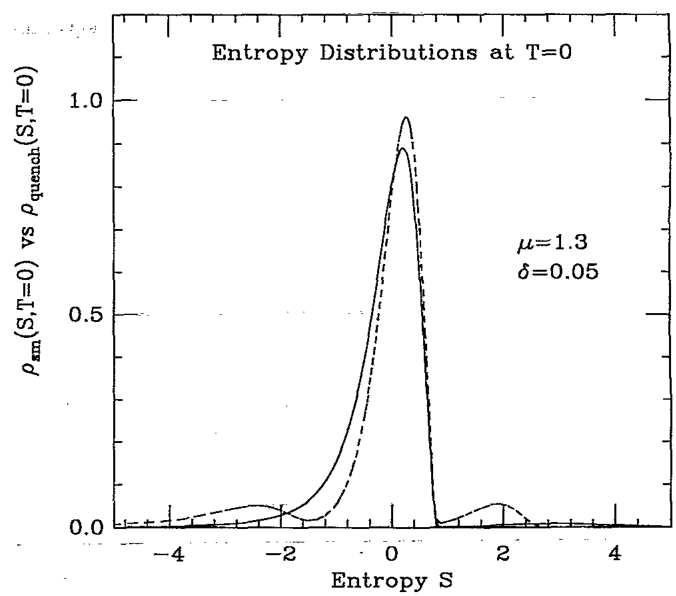

FIG. 5. Zero-temperature entropy distribution for smooth cooling schedule $T_{sm}(t)$ with $\delta=0.05$ and $\mu=1.3$ as calculated by the zeroth-order uniform solution. The weaker peak at higher entropy represents the entropy distribution for TLS's with particles at the upper well at zero temperature. The dashed curve is the zero-temperature entropy distribution when the TLS ensemble is quenched from $T_1=2.0T^*$ to $T_2=1.0T^*$. $k_B\equiv 1$.

develops a hole for the lower-level entropy distribution peak. This has also been observed in the Monte Carlo simulation on TLS's (Ref. 9) and on a small lattice of spin glass.[8] This hole reflects in part the lack of transitions with $\Delta S = \beta\epsilon$ from the upper to the lower well between $\beta_1\epsilon$ and $\beta_2\epsilon$. The spin glass behaved similarly because it had two low-lying states.

The history dependence of the TLS entropy distribution can also be described through linear response. For a cooling schedule around the smooth cooling schedule $T_{\rm sm}(t)$ described by $\beta(t) = \beta_{\rm sm}(t) + \delta\beta(t)$, we have

$$\rho(S,x) = \rho_{\rm sm}(S,x) + \int_x^1 dx_1 \frac{d\delta\beta}{dx_1} \mathcal{H}(S,x_1,x) , \tag{19}$$

where the linear-response kernel $\mathcal{H}(S,x_1,x)$ physically represents the change of the entropy distribution due to an infinitesimal quench as depicted in Fig. 2. We derive the form for $\mathcal{H}$ in Appendix B.

The linear-response kernel qualitatively describes the hole in Fig. 5, despite the factor of 2 shift in temperature. In Fig. 6 we compare our asymptotic analysis for a 10% jump with the linear-response prediction. The jump from $1.05T^*$ to $0.95T^*$ is in the most sensitive region. One can see from the plot that the physical effect of a temperature quench of 10% of the freezing temperature T^* is still in the linear-response regime.

We have shown that the history dependence of the two-level system can be understood through the linear response of its physical properties with respect to variations in its thermal history. We have calculated the linear responses of the two-level system energy, entropy, and entropy distributions.

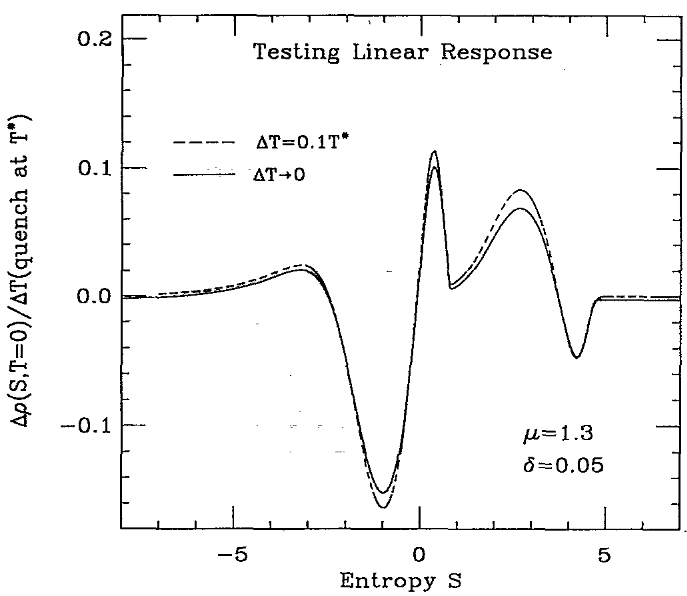

FIG. 6. Linear response of the zero-temperature entropy distribution $\lim_{\Delta T\to 0} \Delta\rho(S,T=0)/\Delta T$ (solid line) to an infinitesimal quench at $T_q = T^*$ as compared with the finite-temperature quench response of the zero-temperature entropy distribution $\Delta\rho(S,T=0)/\Delta T$ (dashed line) for TLS's with $\delta = 0.05$, $\mu = 1.3$, and $\Delta T = 0.1T^*$. The two responses are roughly the same, which shows the large range of validity of the linear-response description. $k_B \equiv 1$.

ACKNOWLEDGMENTS

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APPENDIX A: ASYMPTOTIC SOLUTIONS OF TLS ENTROPY DISTRIBUTION FOR COOLING SCHEDULE $T_{\rm sm}(t)$

In this appendix we will first briefly summarize the definitions, master equations, and asymptotic solutions for the entropy distributions with cooling schedule $T_{\rm sm}(t)$ as obtained by Langer *et al.* Then we will make some necessary improvements of these earlier asymptotic solutions and set up the procedures of obtaining uniform solutions of the entropy distributions of TLS's under cooling schedule $T_{\rm sm}(t)$.

Following Langer *et al.*, consider an ensemble of identical TLS's (same ϵ and V) with identical thermal histories [same $T(t)$]. Each TLS has its own time evolution, making transitions and exchanging energy $\Delta Q = \pm\epsilon$ with the heat bath at various temperatures. So each will have its own entropy $S(T(t)) = \ln 2 - \int dt\, \dot{Q}(t)/T(t)$. We can describe the ensemble by introducing the distribution of the measured thermodynamic entropies $\rho(S)$. The entropy distribution can be further split into two parts, $\rho_\uparrow(S,T)$ and $\rho_\downarrow(S,T)$, representing the probabilities of finding the system in either the upper or lower well, and simultaneously measuring the entropy to be between S and $S+dS$. Obviously,

$$\rho(S,T) = \rho_\uparrow(S,T) + \rho_\downarrow(S,T) . \tag{A1}$$

The master equations for the evolution of the entropy distribution are[8]

$$\begin{aligned} \frac{\partial\rho_\uparrow(S,T)}{\partial t} &= -\Gamma_{\uparrow,\downarrow}(T)\rho_\uparrow(S,T) + \Gamma_{\downarrow,\uparrow}(T)\rho_\downarrow(S-\beta\epsilon,T) , \\ \frac{\partial\rho_\downarrow(S,T)}{\partial t} &= \Gamma_{\uparrow,\downarrow}(T)\rho_\uparrow(S+\beta\epsilon,T) - \Gamma_{\downarrow,\uparrow}(T)\rho_\downarrow(S,T) . \end{aligned} \tag{A2}$$

The initial entropy distribution is naturally chosen as

$$\rho_\uparrow(S,T=\infty) = \rho_\downarrow(S,T=\infty) = \tfrac{1}{2}\delta(S-\ln 2) . \tag{A3}$$

Let us suppose that the TLS ensemble we will consider is smoothly cooled to zero temperature according to a cooling schedule $T(t)$. At high temperatures the TLS ensemble is nearly in equilibrium and the entropy distribution will be two sharp peaks separated by $\beta\epsilon$. The upper peak is $\rho_\uparrow$ and the lower peak is $\rho_\downarrow$. They will move apart and remain sharp as long as the temperature is high enough. As we lower the temperature, the peaks start to broaden and the TLS falls out of equilibrium at around the "freezing" temperature T^*. Near and below T^* the two entropy distribution peaks will not be able to move fast enough to maintain their equilibrium separation and magnitudes. The transitions between the upper and lower levels will transfer an entropy $\beta\epsilon > \beta^*\epsilon$, creating long tails for the two peaks. In Ref. 8 Langer, Dorsey, and Sethna solved the entropy distribution master equations (A2) with asymptotic expansion for the cooling schedule $T_{\rm sm}(t)$ and found

$$\frac{\tilde{\rho}_\uparrow(\sigma,x)}{\tilde{\rho}_\downarrow(\sigma,x)}=x_0^{\mu(1-i\sigma)}e^{x/x_0}\Gamma\left[1+\mu(1-i\sigma),\frac{x}{x_0}\right], \quad (A4)$$

and

$$\ln[\tilde{\rho}_\uparrow(\sigma,x)\tilde{\rho}_\downarrow(\sigma,x)] =f(\sigma)-\frac{1}{x_0}\int_x^1 dz\left[1+z^\mu-z^{\mu(1-i\sigma)}\frac{\tilde{\rho}_\downarrow(\sigma,x)}{\tilde{\rho}_\uparrow(\sigma,x)} -z^{i\sigma\mu}\frac{\tilde{\rho}_\uparrow(\sigma,x)}{\tilde{\rho}_\downarrow(\sigma,x)}\right], \quad (A5)$$

where the function $f(\sigma)$ depends on the initial high-temperature distribution and is $2(i\sigma-1)\ln 2$ for the choice of Eq. (A3), $x\equiv x(T)=e^{-\beta V}$, $x_0=\delta=RV/\Gamma_0T_0$, $\mu=\epsilon/V$, and $\tilde{\rho}_{\uparrow,\downarrow}(\sigma,x)$ is the Fourier transform of the entropy distribution $\rho_{\uparrow,\downarrow}(S,T)$. As shown in Ref. 8, these solutions agree well with the Monte Carlo simulations and they have captured the basic physics of TLS entropy distributions. But, strictly speaking, these solutions are not uniform solutions as the cooling rate $\delta\rightarrow 0$, since although Eq. (A4) is the zeroth-order uniform solution, Eq. (A5) is not the zeroth-order uniform solution because of the $1/x_0$ term in front of the integral. As a result of this, e.g., the upper-level population n deduced from these solutions will not approach the equilibrium population as $\delta\rightarrow 0$. Before we study the history dependence of the TLS entropy distribution, we need to write down the correct zeroth-order asymptotic solutions of the entropy distribution for the cooling schedule $T_{\rm sm}(t)$. For more details about the asymptotic expansion method used here, we refer readers to Refs. 8 and 14.

Briefly, by a change of the variables

$$\psi(\sigma,x)=\ln[\tilde{\rho}_\downarrow(\sigma,x)/\tilde{\rho}_\uparrow(\sigma,x)]-i\sigma\mu\ln x , \quad (A6)$$

Eq. (A2) can be rewritten as

$$\delta\frac{\partial\psi}{\partial x}=x^\mu(1+e^\psi)-(1+e^{-\psi})-\delta\frac{i\sigma\mu}{x}, \quad (A7)$$

and

$$\ln\tilde{\rho}_\downarrow(\sigma,x)=(i\sigma-1)\ln 2-\frac{1}{\delta}\int_x^1 dz(z^\mu-e^{-\psi(\sigma,z)}) . \quad (A8)$$

Since the experimental time scale is much larger than the microscopic attempt time scale $1/\Gamma_0$, we can try to solve the above equations in the limit $\delta\equiv VR/T_0\Gamma_0\ll 1$. As one can see from Eq. (A8), in order to obtain the zeroth order (in δ) uniform solutions of the entropy distribution functions $\tilde{\rho}_{\uparrow,\downarrow}(\sigma,x)$, we need to obtain the *first*-order uniform solution of ψ by solving Eq. (A7).

In the equation for ψ, the highest derivative term $d\psi/dx$ is multiplied by a small parameter δ. The solution of ψ develops a region of a rapid variation around $x=0$, which is called the boundary layer (or inner region). Physically, the inner region corresponds to the low-temperature region with temperature below and around the freezing temperature T^*. In order to obtain a solution that is uniform in all x, we need to treat the high-temperature region (outer region) and the low-temperature region (inner region) separately and match them in the intermediate region. Specifically, in the high-temperature region, the TLS is nearly in equilibrium, and so we can treat the slow cooling rate parameter δ perturbatively by expanding the high-temperature solution in powers of δ. In the low-temperature region, we will rescale the variable x into $X\equiv x/x_0$ and choose x_0 to make the new highest-derivative term couple to a number of order 1. Then we will treat X as of order 1 and expand the rescaled equation in orders of a small parameter related with x_0. The high- and low-temperature solutions are then matched in the intermediate region characterized by $x_0\ll x\ll 1$.

At high temperatures a valid expression for ψ is obtained by expanding in powers of δ:

$$\psi_{\rm high}=\sum_{k\geq 0}\delta^k\psi_k . \quad (A9)$$

From proof by induction we can show that the high-temperature expansion of ψ can also be written as

$$\psi_{\rm high}=-\mu\ln x+\sum_{n=1}^{\infty}\frac{\delta^n}{x^n}\sum_{m=0}^{\infty}a_{nm}x^{\mu m} . \quad (A10)$$

The second form of high-temperature expansion (A10) will be useful when we need to match it with the low-temperature expansion.

For the low-temperature expansion, let $X\equiv x/x_0$, $\Psi(X)\equiv\psi(x)$ with x_0 to be determined later by making the coefficient of the $\partial\Psi/\partial X$ term of order 1. We have $x_0=\delta$ and

$$\frac{d\Psi}{dX}=x_0^\mu X^\mu(1+e^\Psi)-(1+e^{-\Psi})-\frac{i\sigma\mu}{X} . \quad (A11)$$

The correct form of expansion of Ψ is

$$\Psi(X)=-\ln x_0^\mu+\sum_{k\geq 0}x_0^{\mu k}\Psi_k(X) . \quad (A12)$$

The zeroth-order uniform solution of ψ can be obtained easily, with

$$\psi^{(0)}_{\rm high}(x)=-\mu\ln x , \quad (A13)$$

and

$$\Psi^{(0)}_{\rm low}=-\mu\ln x_0-X-i\sigma\mu\ln X -\ln[\Gamma(1+\mu(1-i\sigma),X)] , \quad (A14)$$

we have

$$\psi^{(0)}_{\rm unif}(x)=\Psi^{(0)}_{\rm low}(X)+\psi^{(0)}_{\rm high}(x)-\psi^{(0)}_{\rm match}(x) =\Psi^{(0)}_{\rm low}(X) , \quad (A15)$$

which gives the ratio of the zeroth-order uniform solution of the Fourier-transformed entropy distribution

$$\frac{\tilde{\rho}^{(0)}_{\uparrow\rm unif}(\sigma,x)}{\tilde{\rho}^{(0)}_{\downarrow\rm unif}(\sigma,x)}=x_0^{\mu(1-i\sigma)}e^{x/x_0}\Gamma\left[1+\mu(1-i\sigma),\frac{x}{x_0}\right] . \quad (A16)$$

But unlike the zeroth-order uniform solution of ψ, the

nth-order (with $n \geq 1$) uniform solution is much more difficult to obtain, and the form of its expression depends on the asymmetry μ because the number of terms of low-temperature expansion in Eq. (A12) we should include depends on the asymmetry μ. This means that we cannot write down a single expression for the first-order uniform solution of ψ (and thus the zeroth-order uniform solutions of the entropy distributions) valid for all asymmetries μ. We can, though, for a given asymmetry μ, solve the nth order uniform solutions of ψ systematically as follows: Assume $n/(m+1) < \mu \leq n/m$; take the high-temperature expansion to order x_0^n as

$$\psi_{\text{high}}^{(n)}(x) = \sum_{k=0}^{n} x_0^k \psi_k(x) . \quad \text{(A17)}$$

Next, take the low-temperature expansion (A12) to order $x_0^{\mu m}$ as

$$\Psi_{\text{low}}^{(n)}(X) = -\mu \ln x_0 + \sum_{k=0}^{m} x_0^{\mu k} \Psi_k(X) . \quad \text{(A18)}$$

$\psi_k(x)$ [or $\Psi_k(X)$] can be solved by putting $\psi_{\text{high}}^{(n)}(x)$ [or $\Psi_{\text{low}}^{(n)}(X)$] back into the equation for ψ (A7) [or for Ψ (A11) and match each order of x_0 (or x_0^{μ}). The two expressions can then be matched in the region $x_0 \ll x \ll 1$ to give the nth-order uniform solution. To ensure matching in the whole region $x_0 \ll x \ll 1$ for every order of x_0, the following technical observation is important. Every low-temperature expansion term $\Psi_k(X)$ exactly matches into an infinite series of the high-temperature expansion terms as

$$x_0^{\mu} \Psi_k(X) = \sum_{n=1}^{\infty} a_{nk} x^{\mu k} \frac{x_0^n}{x^n} . \quad \text{(A19)}$$

We will now simply write down the first-order uniform solution of ψ for $\mu > 1$ and for $\frac{1}{2} < \mu \leq 1$. For $\mu > 1$,

$$\psi_{\substack{\text{unif}\\ \mu>1}}^{(1)}(x) = \Psi_{\text{low}}^{(0)}(X) + \mu(1-i\sigma) x_0 \frac{x^{\mu-1}}{1+x^{\mu}} , \quad \text{(A20)}$$

and the zeroth-order uniform solution for $\tilde{\rho}_{\downarrow}(\sigma,x)$ is

$$\ln \tilde{\rho}_{\substack{\downarrow\text{unif}\\ \mu>1}}^{(0)}(\sigma,x) = (i\sigma - 1)\ln 2 - \frac{1}{x_0}\int_x^1 dz \{ z^{\mu} - \exp[-\psi_{\text{unif}}^{(1)}(\sigma,z)] \} . \quad \text{(A21)}$$

For $\frac{1}{2} < \mu \leq 1$, the first-order uniform solution of ψ is

$$\psi^{(1)}{}_{\substack{\text{unif}\\ 1/2<\mu\leq 1}}(x) = \Psi_{\text{low}}^{(0)}(X) + x_0^{\mu} \Psi_1(X) - \mu(1-i\sigma)\frac{x_0}{x}\frac{x^{2\mu}}{1+x^{\mu}} , \quad \text{(A22)}$$

where

$$\Psi_1(X) = -\frac{1}{\tilde{\Gamma}(X)} \int_X^{\infty} dX_1 [X_1^{\mu} - e^{X_1} X_1^{i\sigma\mu} \tilde{\Gamma}(X_1)] \tilde{\Gamma}(X_1) , \quad \text{(A23)}$$

with

$$\tilde{\Gamma}(X) \equiv \Gamma(1+\mu(1-i\sigma), X) . \quad \text{(A24)}$$

We have now set up the correct procedure of obtaining uniform solutions of the TLS entropy distributions for the smooth cooling schedule $T_{\text{sm}}(t)$ using the dimensionless cooling rate δ as a small parameter. For asymmetry $\mu > 1$ we have written down the explicit expression of the zeroth-order uniform solutions in Eqs. (A16) and (A21). The zero-temperature entropy distribution for the smooth cooling schedule $T_{\text{sm}}(t)$ calculated from these two equations with $\mu = 1.3$ and $\delta = 0.05$ is shown in Fig. 5 (in solid line).

APPENDIX B: ENTROPY DISTRIBUTION HISTORY DEPENDENCE LINEAR-RESPONSE KERNELS

Having studied the entropy distribution of TLS's for the smooth cooling schedule $T_{\text{sm}}(t)$, we will now study the history dependence of the TLS entropy distribution through linear response. Again, we represent the perturbation of thermal history by $\beta(t) = \beta_{\text{sm}}(t) + \delta\beta(t)$. Without details of the calculations, we write down the results of the entropy distribution linear response as

$$\rho_{\uparrow,\downarrow}(S,x) = \rho_{\uparrow,\downarrow\text{sm}}(S,x) + \int_x^1 dx_1 \frac{d\delta\beta}{dx_1} \mathcal{K}_{\uparrow,\downarrow}(S,x_1,x) , \quad \text{(B1)}$$

where the linear-response kernels $\mathcal{K}_{\uparrow,\downarrow}(S,x_1,x)$ can be calculated exactly if we know $\rho_{\uparrow,\downarrow\text{sm}}(S,x)$. But since $\rho_{\uparrow,\downarrow\text{sm}}(S,x)$ can be calculated only approximately, we have to decide how precise the approximate solution of

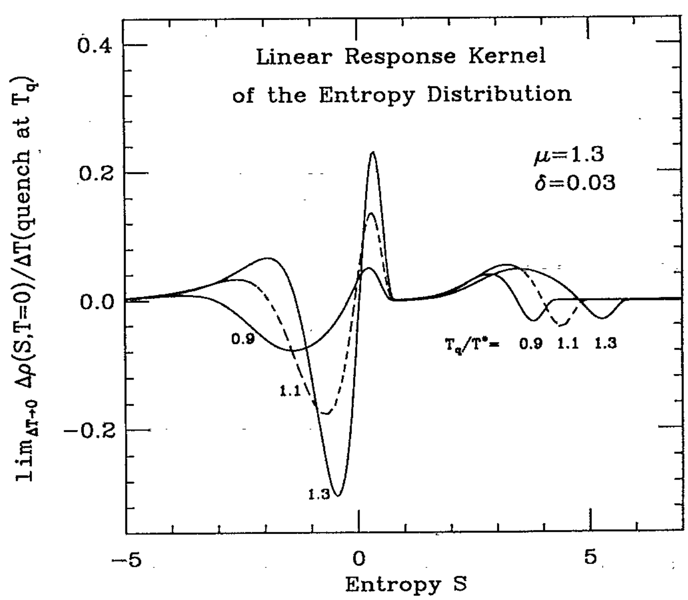

FIG. 7. Linear response of the TLS ($\mu = 1.3$, $\delta = 0.03$) zero-temperature entropy distribution with respect to small quenches at $T = 0.9T^*$, $1.1T^*$, and $1.3T^*$. $k_B \equiv 1$.

$\rho_{\uparrow,\downarrow\mathrm{sm}}(S,x)$ that we take should be for us to have a uniform solution of the entropy distribution linear-response kernel $\mathcal{K}_{\uparrow,\downarrow}(S,x_1,x)$. It is easy to show that if we want to find the nth-order uniform solution of kernels $\mathcal{K}_{\uparrow,\downarrow}(S,x_1,x)$, we need the $(n+1)$th-order uniform solutions of $\rho_{\uparrow,\downarrow\mathrm{sm}}(S,x)$. So far, we are only able to compute numerically the zeroth-order uniform solution of $\rho_{\uparrow,\downarrow\mathrm{sm}}(S,x)$, although we can write down the complicated analytic solution for the first-order uniform solution of $\rho_{\uparrow,\downarrow\mathrm{sm}}(S,x)$. Fortunately, the physically interesting regions are around and below the freezing temperature, because thermal fluctuations will wash away the TLS's memory of the high-temperature thermal history and the TLS's are always very close to equilibrium at such high temperatures. So long as both the quench temperature and the final temperature are within the domain of validity $x \lesssim x_0$ of the low-temperature expansion, the calculations of kernels $\mathcal{K}_{\uparrow,\downarrow}(S,x_1,x)$ can be simplified, and getting the nth-order uniform solutions of the kernels only requires knowing the nth-order uniform solutions of $\rho_{\uparrow,\downarrow\mathrm{sm}}(S,x)$. The zeroth-order uniform solution of the entropy distribution history dependence linear-response kernels for $x \le x_0$ can be written through their Fourier transforms as

$$\tilde{\mathcal{K}}_{\downarrow}(\sigma,x_1,x)=\tilde{\rho}_{\downarrow\mathrm{sm}}(\sigma,x)x_0^{\mu}VX_1[\Gamma(1+\mu(1-i\sigma),X_1)-X_1^{\mu(1-i\sigma)}e^{-X_1}]\left[X_1^{i\sigma\mu}e^{X_1}-\int_X^{X_1}dZ\,Z^{i\sigma\mu}e^{Z}\right], \tag{B2}$$

and

$$\tilde{\mathcal{K}}_{\uparrow}(\sigma,x_1,x)=\tilde{\rho}_{\uparrow\mathrm{sm}}(\sigma,x)\left[\frac{\tilde{\mathcal{K}}_{\downarrow}(\sigma,x_1,x)}{\tilde{\rho}_{\downarrow\mathrm{sm}}(\sigma,x)}-VX_1\frac{\Gamma(1+\mu(1-i\sigma),X_1)-X_1^{\mu(1-i\sigma)}e^{-X_1}}{\Gamma(1+\mu(1-i\sigma),X)}\right], \tag{B3}$$

where $X\equiv x/x_0$. We can numerically calculate the linear response of the entropy distribution with respect to a small quench at various temperatures during cooling. This linear response is represented by $\mathcal{K}_{\uparrow,\downarrow}(S,x_1,x)$ through the following relation: For the smooth cooling schedule with a small quench at temperature T_q as described by Eq. (12), the change of entropy distribution at zero temperature due to a quench of temperature at T_q is

$$\lim_{\Delta T\to 0}\frac{\Delta\rho(S,T=0)}{\Delta T}=\frac{d\beta_q}{dT_q}[\mathcal{K}_{\uparrow}(S,x_q,0)+\mathcal{K}_{\downarrow}(S,x_q,0)]\,. \tag{B4}$$

In Fig. 7 we have plotted this linear response for quenches at a few different temperatures around the freezing temperature T^*. A few observations can be made about these plots: (1) For quenches at higher temperatures, the upper- and lower-level entropy distribution response peaks are closer. This is because the upper- and lower-level entropy distribution peaks are separated roughly by $\Delta S=\epsilon/T_q$ at temperature T_q before the quench. Therefore, the upper- and lower-level entropy distribution responses to the perturbation of quenching are also separated roughly by $\Delta S=\epsilon/T_q$ and remain so when the TLS ensemble is cooled to zero temperature. (2) The upper-level entropy distribution response is mostly positive with a small dip. Just after the quench from x_q to $x_q-\Delta x$, the change in the entropy distribution $(d\beta_q/dT_q)\mathcal{K}(S,x_q,x_q-\Delta x)$ reflects the transitions that would have occurred during the temperature range skipped. Since the system is more or less out of equilibrium, most of these transitions would have been from the upper to the lower level: Hence the upper peak gains population from the quench and the response is largely positive. Since the lower peak is skewed to the right and the upper peak is skewed slightly to the left, the few uphill transitions missed produce a small dip on the right. (3) The lower-level entropy distribution response is larger than that of the upper level and looks like its negative plus an extra bump at the leftmost end. As we cool the TLS's smoothly from $x_q-\Delta x$ to zero temperature, much of the upper-level population will shift to the lower level, shrinking the upper-level response without changing its shape. These transfer to the lower level peak *at a lower temperature* than T_q, and so instead of partially canceling the lower-level peak, they build up a bump on the left. (4) The upper-level entropy distribution response is the strongest at around $x_{\uparrow}^*\approx x_0$, and the lower-level entropy distribution response is the strongest at around $x_{\downarrow}^*\approx x_0^{1+\mu}$. (This particular feature of the lower-level response could not be put in Fig. 7, but is true.) In short, this is due to the fact that the upper- to lower-level transition has a smaller barrier (V) than the lower- to upper-level transitions ($V+\epsilon$).

As shown above, the zero-temperature entropy distributions remember the TLS's cooling history, and the entropy distribution responds to small temperature quenches at different temperatures differently. The linear response of the zero-temperature entropy distribution is the strongest if the temperature quench happens around the freezing temperature.

APPENDIX C: TLS ENTROPY DISTRIBUTION UNDER A COOLING SCHEDULE WITH FINITE-TEMPERATURE QUENCH

Since the physically interesting temperature region is around the freezing temperature, we will only derive the formula for the entropy distribution of TLS's ($\mu>1$) under a quenched cooling schedule as given by Eq. (12) with $T_1 \sim T_2 \sim O(T^*)$. As we cool the TLS's from $T=\infty$ to T_1, before the quench, the entropy distribution should be the same as the solution we had for the smooth cooling schedule $T_{\rm sm}(t)$. Thus, for $\mu>1$, $T>T_1$, $\tilde{\rho}^{(0)}_{\uparrow\rm unif}(\sigma,x)/\tilde{\rho}^{(0)}_{\downarrow\rm unif}(\sigma,x)$ is determined by Eq. (A16) and $\tilde{\rho}^{(0)}_{\downarrow\rm unif}(\sigma,x)$ is determined by Eq. (A21). After the quench the TLS's are cooled through the low-temperature region, and the zeroth- as well as the first-order solution for ψ after the quench is

$$\Psi^{(0),(1)}_{\rm low}(X)=-\mu\ln x_0-X-i\sigma\mu\ln X-\ln[F^{(0),(1)}(\sigma)+\Gamma(1+\mu(1-i\sigma),X)]\ . \tag{C1}$$

So we have

$$\frac{\tilde{\rho}^{(0),(1)}_{\uparrow AQ}(\sigma,x)}{\tilde{\rho}^{(0),(1)}_{\downarrow AQ}(\sigma,x)}=x_0^{\mu(1-i\sigma)}e^{x/x_0}\left[F^{(0),(1)}(\sigma)+\Gamma\left[1+\mu(1-i\sigma),\frac{x}{x_0}\right]\right],\quad \text{for } T\le T_2\ , \tag{C2}$$

where the subscript "AQ" stands for "after quench" and $F(\sigma)$ is determined by the fact that $\tilde{\rho}_{\uparrow,\downarrow}(\sigma,x)$ is the same immediately before and after the quench. We have

$$F^{(0)}(\sigma)=\exp\left[\frac{x_1-x_2}{x_0}\right]\Gamma\left[1+\mu(1-i\sigma),\frac{x_1}{x_0}\right]-\Gamma\left[1+\mu(1-i\sigma),\frac{x_2}{x_0}\right]\ , \tag{C3}$$

and

$$F^{(1)}(\sigma)=\exp\left[\frac{x_1-x_2}{x_0}\right]\exp\left[-\mu(1-i\sigma)x_0\frac{x_1^{\mu-1}}{1+x_1^{\mu}}\right]\Gamma\left[1+\mu(1-i\sigma),\frac{x_1}{x_0}\right]-\Gamma\left[1+\mu(1-i\sigma),\frac{x_2}{x_0}\right]\ . \tag{C4}$$

From the formula above the zeroth-order uniform solution of the TLS ($\mu>1$) entropy distribution under a quenched cooling schedule with $T_1\sim T_2\sim T^*$ is

$$\frac{\tilde{\rho}^{(0)}_{\uparrow\rm unif}(\sigma,x)}{\tilde{\rho}^{(0)}_{\downarrow\rm unif}(\sigma,x)}=\begin{cases} x_0^{\mu(1-i\sigma)}e^{x/x_0}\Gamma(1+\mu(1-i\sigma),x/x_0) & \text{for } T>T_1\ ,\\ x_0^{\mu(1-i\sigma)}e^{x/x_0}[F^{(0)}(\sigma)+\Gamma(1+\mu(1-i\sigma),x/x_0)] & \text{for } T<T_2\ ,\end{cases} \tag{C5}$$

and

$$\ln\tilde{\rho}^{(0)}_{\downarrow\rm unif}(\sigma,x)=(i\sigma-1)-\frac{1}{x_0}\int_{x_1}^{1}dz\{z^{\mu}-z^{i\sigma\mu}\exp[-y^{(1)}_{\rm unif}(\sigma,z)]\}-\frac{1}{x_0}\int_{x}^{x_2}dz\left[z^{\mu}-z^{i\sigma\mu}\frac{\tilde{\rho}^{(0)}_{\uparrow\rm AQ}(\sigma,z)}{\tilde{\rho}^{(0)}_{\downarrow\rm AQ}(\sigma,z)}\right]\quad\text{for } T<T_2\ . \tag{C6}$$

[1]See, e.g., A. J. Esteal *et al.*, J. Am. Ceram. Soc. **60**, 134 (1977); C. T. Moynihan *et al.*, *ibid.* **59**, 12 (1976).
[2]See, e.g., G. W. Scherer, *Relaxation in Glass and Composites* (Wiley, New York, 1986), p. 122. The data are from H. N. Ritland, J. Am. Ceram. Soc. **37**, 370 (1954).
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[11]See Scherer, Ref. 2, p. 123. The data are from Ritland (Ref. 2). Using the density of glass as criterion, the rate of change of the fictive temperature of the glass is about 19 K for a change in cooling rate of a factor of 10.
[12]As an example, $\mathcal{N}(x_q,x)$ is closely related to the time-dependent specific heat. The finite-frequency specific heat measured around a fixed temperature [as done by Birge and Nagel (Ref. 13) for glycerol] for the TLS is simply related to the upper-level population linear-response kernel $\mathcal{N}(x_1,x)$ through

$$C(\omega,T)=\epsilon\frac{dn_{\rm eq}(T)}{dT}-\frac{i\omega\epsilon}{T^2}\int_{-\infty}^{0}dt'e^{-i\omega t'}\times\lim_{\delta\to 0}\mathcal{N}(x_{\rm sm}(t+t'),x_{\rm sm}(t)=x(T))\ .$$

The limit $\delta \to 0$ reflects the fact that Birge and Nagel work in equilibrium. From Eq. (11) it is easy to obtain

$$C(\omega,T)=\epsilon\frac{dn_{eq}(T)}{dT}\frac{1}{1-i\omega/\Gamma_0 x(1+x^{\mu})}\ .$$

It is in fact much easier to obtain this result directly by solving Eq. (3). The characteristic frequency at temperature T is $\omega(T)=\Gamma_0 x(T)[1+x(T)^{\mu}]$. For $\omega \gg \omega(T)$, the TLS degree of freedom is effectively frozen.

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