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Entropy distribution of a two-level system: An asymptotic analysis

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Although glasses are not in equilibrium, for some purposes they are nearly in equilibrium. The thermodynamic properties of glasses depend on their thermal history, and when the time scale of this history is long compared to the microscopic time scale of the glass, we can compute thermodynamic quantities. In this paper, we use matched asymptotic expansions to compute the energy and entropy distribution of the simplest possible model glass, a single two-level system, in the limit of slow heating and cooling.

I. INTRODUCTION

Glasses are not in equilibrium. The material properties of a glass depend upon its entire thermal history. Liquids and crystals can be approximated as equilibrium systems because of a separation of time scales: We can average over the fast degrees of freedom and ignore the slow ones. In glasses, processes take place on a wide range of time scales, spanning the time scale of the experiment.[1] On the other hand, there is a separation of time scales in glasses too. Although the time for transitions between microscopic states can be very long, very short, or in between, the microscopic *attempt* time for transitions is always very short, about 10^{-12} s. The macroscopic time scale of an experiment, involving, say, cooling a glass from the melting point to zero temperature, is at least on the order of seconds, much longer than the microscopic time. We can consider the glass to be a system not far from equilibrium, in the sense that it has tried many routes to relaxation, and we can exploit this separation of time scales in calculations.

The equilibrium properties of ensembles of two-level systems are often used to model the low-temperature properties of glasses.[2,3] In this paper, however, we use a two-level system (TLS) as a model for high-temperature glassy *dynamical* properties. A TLS is in some sense the simplest possible model glass. It has a wide range of time scales because the transition rate depends strongly on the temperature. It is glasslike because (1) it falls out of equilibrium when the cooling rate becomes fast compared to the transition rate, (2) when out of equilibrium it has multiple zero-temperature states, and (3) its properties depend on its thermal history. It is simple because it has only one degree of freedom, the energy, which can be either 0 or ε. The model is, of course, too simple to explain many properties of real glasses, such as nonexponential relaxation and the Kauzmann paradox. In this paper we use a separation of time scales to compute the average energy of an ensemble of identical TLS's cooled and heated asymptotically slowly.

A characteristic property of glasses is their nonzero zero-temperature entropy.[4] Entropy can be defined[5] either "statistically,"

$$S_{\text{stat}} = -\operatorname{Tr}\hat{\rho}\ln\hat{\rho} \ , \tag{1}$$

or "thermodynamically,"

$$\Delta S_{\text{therm}} = \int \frac{dQ}{T} \ . \tag{2}$$

$\hat{\rho}$ is the density matrix, Q is the heat flowing into the glass, and T is the temperature. Reference 5 shows that the thermodynamic entropy, measured on heating and cooling, provides upper and lower bounds to the statistical entropy. This is important, because the thermodynamic entropy is accessible in experiments and computer simulations, whereas the statistical entropy, which measures the available volume of phase space, and is usually of greater theoretical interest, is inaccessible. In real experiments, we estimate the difference between the upper and lower bounds to be about 1%.[6] In computer simulations the bounds can differ enormously. Furthermore, the measured thermodynamic entropies of an ensemble of identical TLS's will differ on successive runs of a simulation, even if the TLS's have the identical thermal histories, because transitions between the states of TLS's will take place at different temperatures. These fluctuations create a *distribution* of measured thermodynamic entropies. In a real glass, many TLS's will undergo transitions concurrently, and self-averaging will make the entropy distribution collapse onto its mean. In a computer simulation, however, as shown in Ref. 5, the distribution will have structure indicative of the dynamics of the glass. The structure will be more pronounced the farther the simulation is from equilibrium. In this paper we calculate this entropy distribution for an asymptotically slowly cooled TLS.

The starting points for the energy and entropy calculations are the master equations for the energy and entropy distribution, which we write in a form that makes the separation of time scales obvious. We solve these equations in the limit of asymptotically slow cooling, and compare the results with numerical computations and computer simulations.

II. MASTER EQUATIONS

A TLS, such as the one shown in Fig. 1, can be in one of two states or wells. The energy of the two wells differs by an asymmetry ε, and there is a barrier V to transitions between the wells. We will take V to be measured from the bottom of the upper well to the top of the barrier. In the absence of quantum-mechanical tunneling through the barrier, transitions take place by thermal excitation over the barrier, with a rate given by

$$\Gamma(T)=\Gamma_0 e^{-\beta V}\ , \tag{3}$$

where $\beta=1/T$ is a function of time, t. Consider an ensemble of identical TLS's with identical thermal histories, but with different individual histories [ε, V, and $T(t)$ are the same for each TLS in the ensemble, but each makes transitions independently]. Let $n=n_\uparrow$ be the population of the upper well, averaged over the ensemble. The population of the lower well is $n_\downarrow=1-n$. The energy distribution for the ensemble is

$$\rho(E)=(1-n)\delta(E)+n\delta(E-\varepsilon)\ .$$

The evolution of n is governed by the master equation,

$$\frac{dn}{dt}=\Gamma(T)[e^{-\beta\varepsilon}(1-n)-n]\ . \tag{4}$$

The equilibrium population is

$$n_0(T)=\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}\ .$$

At high temperatures, the transition rate $\Gamma(T)$ is much larger than the rate of change of n_0, and $n(T)\approx n_0(T)$. (See Fig. 2.) At low temperatures $\Gamma(T)$ is very small, so $n(T)$ is nearly constant. The value of n at zero temperature (the "residual" population) is roughly the population of the system at the "freezing" temperature, T^* where the rate of transitions over the barrier is comparable to the cooling rate:

$$\left|\frac{dn_0}{dt}\right|_{T=T^*}\approx\Gamma(T^*)n_0(T^*)\ . \tag{5}$$

When the TLS is now heated from zero temperature, its population remains constant until the transition rate becomes comparable to the heating rate. At this point, the population will be above n_0, so although the temperature is increasing, the population will decrease. The measured specific heat, $\varepsilon dn/dT$, will be negative in this region. As the temperature rises further, n_0 increases, and when it becomes greater than n, n will begin to increase, until $n\lesssim n_0$ at higher temperatures.

We can also write down a master equation for the evolution of the entropy distribution, $\rho(S)$. First, we split the distribution 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[7] measuring the thermodynamic entropy to be between S and $S+dS$. Obviously,

$$\rho(S,T)=\rho_\uparrow(S,T)+\rho_\downarrow(S,T)\ ,$$

and

$$\int_{-\infty}^{\infty}\rho_\uparrow(S,T)dS=n\ .$$

When the system makes a transition from the lower well to the upper well, it absorbs energy ε from the environment, and its thermodynamic entropy increases by $\beta\varepsilon$. Upward transitions therefore deplete $\rho_\downarrow(S,T)$ and contribute to $\rho_\uparrow(S+\beta\varepsilon,T)$. Similarly, downward transitions deplete $\rho_\uparrow(S,T)$ and contribute to $\rho_\downarrow(S-\beta\varepsilon,T)$. The coupled master equations are

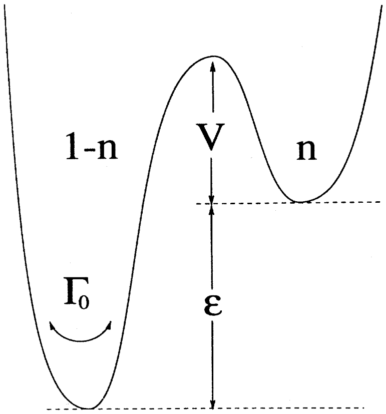

FIG. 1. A two-level system, showing the barrier height V and asymmetry ε. The ensemble average population of the upper well is n, and the small oscillation frequency in the bottom of the wells is Γ_0.

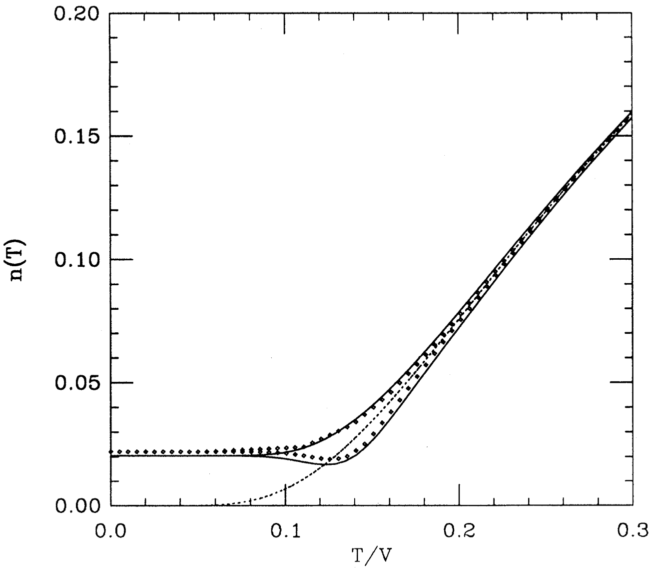

FIG. 2. Population vs temperature (Ref. 12) for TLS with asymmetry $\mu=0.5$ cooled linearly to zero temperature with cooling rate $\delta=10^{-5}$ and then heated at the same rate. The data points are the result of direct numerical integration of (4), and the solid lines are the asymptotic expressions, with $x_0=\delta(\ln x_0)^2$. The dashed line is the equilibrium population, n_0.

$$\begin{aligned}\frac{\partial\rho_\uparrow(S,T)}{\partial t}&=\Gamma(T)[-\rho_\uparrow(S,T)+e^{-\beta\varepsilon}\rho_\downarrow(S-\beta\varepsilon,T)]\ ,\\ \frac{\partial\rho_\downarrow(S,T)}{\partial t}&=\Gamma(T)[\rho_\uparrow(S+\beta\varepsilon,T)-e^{-\beta\varepsilon}\rho_\downarrow(S,T)]\ .\end{aligned}\tag{6}$$

Unlike the master equation for the population, (6) does not completely determine its own equilibrium solution. This is because the thermodynamic entropy is only defined up to an additive constant, and, in principle, the constant could have been chosen differently for each TLS in the ensemble. In other words, (6) determines the evolution of an arbitrary initial entropy distribution. When we need to specify an initial condition, we will make the natural choice:[8]

$$\rho_\uparrow(S,\ T=\infty)=\rho_\downarrow(S,\ T=\infty)=\tfrac{1}{2}\delta(S-\ln 2)\ .\tag{7}$$

What happens to the entropy distribution as the ensemble of TLS's is cooled to zero temperature at a nonzero rate? (See Fig. 3.) At high temperatures, where the transition rate is large compared to the cooling rate, the system will be nearly in equilibrium. The entropy distribution will still be sharply peaked, because each TLS in the ensemble will have nearly the same history. However, since transitions between the wells change the entropy, there will be two peaks in the distribution separated by $\beta\varepsilon$. The upper peak is $\rho_\uparrow$ and the lower peak is $\rho_\downarrow$. These peaks will move, but will remain sharp, as long as the transition rate remains high. As the transition rate falls, the degree of self averaging also falls, and the peaks will broaden. Erratic transitions at random temperatures transfer random amounts of entropy. Near the temperature $T^*=1/\beta^*$, where the system "freezes," the peaks will not be able to move fast enough to maintain their equilibrium separation and magnitudes. There will still be transitions from the upper well to the lower well, but they will transfer an entropy $\beta\varepsilon>\beta^*\varepsilon$, so weight in the distribution will move from the upper peak to the low entropy side of the lower peak, creating a long tail. This effect is clearly seen in Fig. 3.

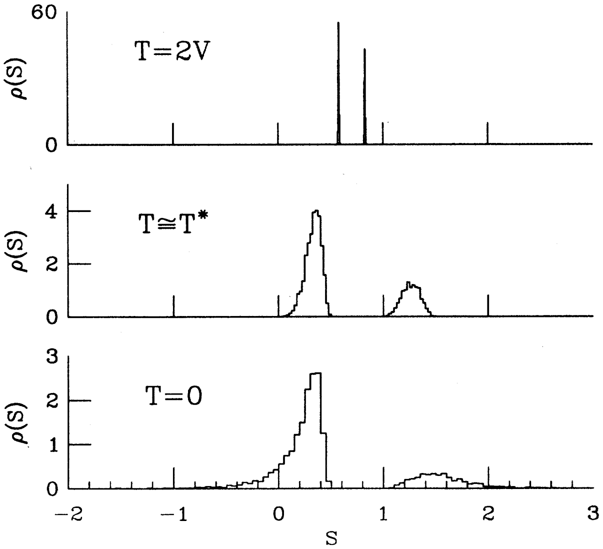

FIG. 3. Entropy distributions from a Monte Carlo simulation of a TLS with asymmetry $\varepsilon=0.5V$ at temperature (a) $T=2V$, (b) $T\gtrsim T^*$, and (c) $T=0$. The cooling rate was $\delta=0.01$.

III. ASYMPTOTIC CALCULATION OF THE ENERGY

The residual population of the TLS was calculated for small cooling rate by Huse and Fisher[9] (see Appendix). Our result is slightly different from theirs; we present our calculation as a prelude to the calculation of the entropy distribution. The first step in the solution of the master equations (4) and (6) is to write them in terms of a dimensionless cooling rate, so as to identify the small parameter. To do this, it is of course necessary to specify the cooling schedule $T(t)$. The easiest choice might seem to be linear cooling, $T(t)=T_0-rt$, but, in fact, the calculations are simplified if we set $T(t)=T_0/(1+Rt)$. This choice does not fundamentally alter the results. The linear cooling schedule is discussed in the Appendix.

Making the change of variables $x=\exp(-\beta V)$, and (following Huse and Fisher) defining a dimensionless asymmetry $\mu=\varepsilon/V$, and a dimensionless cooling rate $\delta=RV/\Gamma_0 T_0$, Eq. (4) becomes

$$\delta\frac{dn}{dx}=-x^\mu+(1+x^\mu)n(x)\ .\tag{8}$$

This equation can of course be integrated directly, but the result is not particularly illuminating, and the method cannot be applied to the entropy distribution. Since we are primarily interested in the limit $\delta\rightarrow 0$, asymptotic analysis is the appropriate technique. (δ is the ratio of the microscopic to macroscopic time scales, so for physical systems, we expect $\delta\lesssim 10^{-12}$.) We begin by finding a high-temperature approximation, $n_{\text{hi}}(x)$, for $n(x)$ by expanding in a power series in δ. Equating powers of δ in (8), we find

$$n_{\text{hi}}(x)=\frac{x^\mu}{1+x^\mu}\left[1+\delta\mu\frac{1}{x(1+x^\mu)^2}+O(\delta^2)\right]\ .\tag{9}$$

There are two things to notice. First, when the cooling rate δ vanishes, we recover the equilibrium value of n, as expected. On the other hand, as $x\rightarrow 0$, the second term in (9) diverges, so it cannot be correct for low temperatures. The size of the divergent region is roughly of order δ.

A standard technique in asymptotic analysis is to rescale the independent variable x by the size x_0 of the divergent region (the "boundary layer").[10] The solution of the original equation was valid where x was $O(1)$, in the so-called "outer" region. The solution to the rescaled equation will be valid when x is $O(x_0)$, in the "inner" region. The appropriate identification of x_0 will result in an equation equivalent to (8), but in which the small parameter appears in a different position, leading to qualitatively different behaviors in the inner and outer regions. Let $X\equiv x/x_0$ and $N(X)\equiv x_0^{-\mu}n(x)$. Then

$$\frac{\delta}{x_0}\frac{dN}{dX}=-X^\mu+(1+x_0^\mu X^\mu)N(X)\ ,\tag{10}$$

and we see that setting $x_0=\delta$ has the desired effect. This is not surprising—we expect the character of the solution to (4) to change at the freezing temperature T^*. Solving (5) for T^* shows that the transition occurs for $x\approx\delta\mu$. Different cooling rates require different choices for x_0 but otherwise lead to substantially the same analysis. [For example, linear cooling requires $x_0=\delta(\ln x_0)^2$; see Appendix.] For this reason, the calculations will be presented in terms of x_0 rather than δ.

The general solution to (10) is

$$N(X)=\exp\left[X+\frac{x_0^\mu}{1+\mu}X^{1+\mu}\right]\times\left[N(0)-\int_0^X e^{-[Y+x_0^\mu Y^{1+\mu}/(1+\mu)]}Y^\mu\,dY\right]. \tag{11}$$

This inner, low-temperature solution must match the outer, high-temperature solution (9) in a region where both are valid. To be precise, we want to adjust the arbitrary constant $N(0)$ in (11) so that

$$\lim_{x\to 0}n_{\text{hi}}(x)=\lim_{X\to\infty}x_0^\mu N(X)\equiv n_{\text{match}}(x)$$

to lowest order in δ. The only choice that prevents (11) from diverging as $X\to\infty$ is

$$N(0)=\int_0^\infty dY\,Y^\mu\exp\left[-Y-\frac{x_0^\mu}{1+\mu}Y^{1+\mu}\right]. \tag{12}$$

Unless the asymmetry μ is very small, we have $x_0^\mu\ll 1$, $N(0)\equiv\Gamma(1+\mu)$, and $N(X)=e^X\Gamma(1+\mu,X)$, or

$$n(x\to 0)=x_0^\mu e^{x/x_0}\Gamma(1+\mu,x/x_0).$$

Combining the low- and high-temperature formulas into one expression, uniformly[10] valid in x, we get (see Fig. 2)

$$\begin{aligned}n(x)&\equiv n_{\text{hi}}(x)+x_0^\mu N(x/x_0)-n_{\text{match}}(x)\\&=x_0^\mu e^{x/x_0}\Gamma(1+\mu,x/x_0)-\frac{x^{2\mu}}{1+x^\mu}.\end{aligned} \tag{13}$$

When $\mu\ll 1$ and $x_0^\mu\approx 1$, Eq. (12) reduces to $N(0)=1/(1+x_0^\mu)$. Therefore, uniformly in μ, the residual zero-temperature population is

$$n(0)=x_0^\mu\Gamma(1+\mu)-\frac{x_0^{2\mu}}{1+x_0^\mu}. \tag{14}$$

Figure 4 shows $n(0)$ plotted as a function of δ, for two different asymmetries, in the case of linear cooling.

The master equation for the population while warming the TLS is identical to that master equation for cooling, except that the sign of δ must be changed:

$$-\delta\frac{dn}{dx}=-x^\mu+(1+x^\mu)n(x). \tag{15}$$

The outer solution does not change, to lowest order in δ, and the inner solution becomes

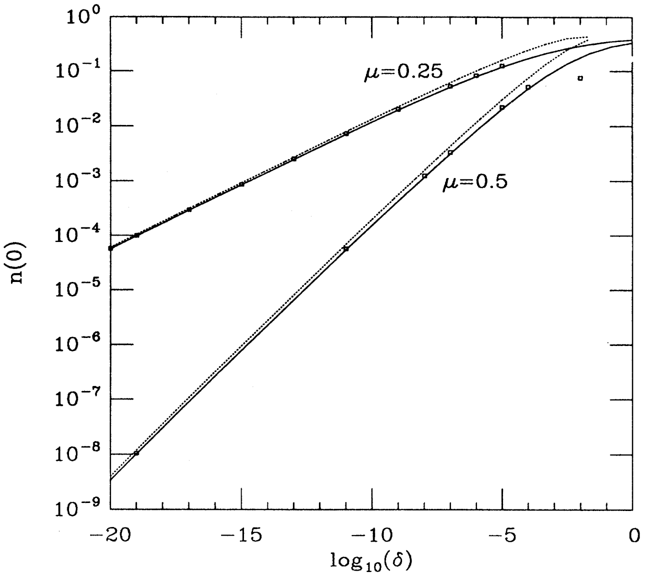

FIG. 4. Residual population vs cooling rate. The solid lines are our asymptotic result (14), the dashed lines are the result of Huse and Fisher (31), and the data points come from numerical integration of (4). All three curves were computed with a linear cooling schedule.

$$N(X)=\exp\left[-X-\frac{x_0^\mu}{1+\mu}X^{1+\mu}\right]\times\left[N(0)+\int_0^X e^{Y+x_0^\mu Y^{1+\mu}/(1+\mu)}Y^\mu dY\right].$$

The inter and outer solutions match as $x\to 0$ and $X\to\infty$ for *any* choice of $N(0)$, as they should, since for warming the population at $T=0$ is a free parameter. The solution uniform in x for μ not too small is

$$n(x)=x_0^\mu e^{-x/x_0}\left[N(0)+\int_0^{x/x_0}e^Y Y^\mu\,dY\right]-\frac{x^{2\mu}}{1+x^\mu}.$$

In Fig. 2, $N(0)$ for the heating curve is given by (14). There is a dip in the heating curve because, initially, at low temperature, the TLS is frozen above equilibrium. As the temperature increases and the TLS thaws, the population relaxes downwards towards its equilibrium value. The minimum population occurs when $n=n_0$, where dn/dt vanishes.

IV. ASYMPTOTIC CALCULATION OF THE ENTROPY DISTRIBUTION

There are two impediments to applying the above analysis directly to the master equations for the entropy distribution (6). The first is that there are two equations, not one, and they cannot be integrated directly, so we will not be able to find an expression like (11). The second and more important problem is that the equations are nonlocal—the distribution at one value of S is linked to the distributions at all others. Both of these problems can be fixed by a judicious change of variables.

The next best thing to computing a distribution function is to compute its cumulants. If $\tilde{\rho}(\sigma,x)$ is the Fourier transform of $\rho(S,x)$, then $\ln\tilde{\rho}(\sigma,x)$ is the generating function for the cumulants κ_n of S. Let

$$\tilde{\rho}_{\uparrow,\downarrow}(\sigma,x)=\int_{-\infty}^{\infty} e^{i\sigma S}\rho_{\uparrow,\downarrow}(S,x)\,dS \ .$$

[The Fourier convention is chosen so that $n(x)=\tilde{\rho}_{\uparrow}(0,x)$.] Then

$$\kappa_n=\frac{1}{i^n}\frac{\partial^n \ln\tilde{\rho}}{\partial\sigma^n}\bigg|_{\sigma=0} ,$$

so that

$$\kappa_1=\langle S\rangle_{\uparrow,\downarrow}$$

and

$$\kappa_2=\langle S^2\rangle_{\uparrow,\downarrow}-\langle S\rangle^2_{\uparrow,\downarrow}$$

and so forth. Define $g_{\uparrow}\equiv\ln\tilde{\rho}_{\uparrow}$, and $g_{\downarrow}\equiv\ln\tilde{\rho}_{\uparrow}$. The master equation (6) for the distributions becomes

$$\delta\frac{\partial g_{\uparrow}}{\partial x}=1-x^{\mu(1-i\sigma)}\exp(g_{\downarrow}-g_{\uparrow}) ,$$

$$\delta\frac{\partial g_{\downarrow}}{\partial x}=x^{\mu}-x^{i\sigma\mu}\exp(g_{\uparrow}-g_{\downarrow}) ,$$

which is simplified further by another change of variables,

$$\begin{aligned} y(\sigma,x)&\equiv g_{\downarrow}(\sigma,x)-g_{\uparrow}(\sigma,x)\\ &\equiv\ln[\tilde{\rho}_{\downarrow}(\sigma,x)/\tilde{\rho}_{\uparrow}(\sigma,x)] , \end{aligned}$$

and

$$z(\sigma,x)\equiv g_{\uparrow}(\sigma,x)+g_{\downarrow}(\sigma,x) ,$$

in terms of which we have

$$\delta\frac{\partial y}{\partial x}=x^{\mu}-1+x^{\mu(1-i\sigma)}e^{y}-x^{i\sigma\mu}e^{-y} , \tag{16}$$

and

$$\delta\frac{\partial z}{\partial x}=x^{\mu}+1-x^{\mu(1-i\sigma)}e^{y}-x^{i\sigma\mu}e^{-y} . \tag{17}$$

The equilibrium distribution function is found by setting $\delta=0$, yielding $y_{\mathrm{eq}}=(i\sigma-1)\mu\ln x$, or

$$\rho_{\downarrow}(S,T)=e^{\beta\varepsilon}\rho_{\uparrow}(S+\beta\varepsilon,T) ,$$

as implied by (6).

An additional advantage to using y and z as the dependent variables is that y has a simple physical interpretation:

$$i\frac{dy}{d\sigma}\bigg|_{\sigma=0}=[\langle S\rangle_{\uparrow}-\langle S\rangle_{\downarrow}]\approx\beta^{*}\varepsilon \tag{18}$$

is the distance between the peaks in the entropy distribution. The distance between the peaks at zero temperature measures the "freezing" temperature T^{*}, as shown earlier.

Furthermore, the initial entropy distribution has dropped out of one equation. At infinite temperature both distributions, $\rho_{\uparrow}(S)$ and $\rho_{\downarrow}(S)$, must be identical. Any initial distribution can be written as a convolution with a delta function,

$$\rho_{\uparrow,\downarrow}(S,x=1)=\int f(S-S')\delta(S'-S^0_{\uparrow,\downarrow})\,dS' ,$$

where f is the same function for both distributions. f appears as a multiplicative function of σ when the distribution is written in terms of the g's and does not appear in y at all. In this sense y is the fundamental object—it contains only information about the evolution and dynamics of the TLS, with the irrelevant initial conditions factored out.

The equations for $y(\sigma,x)$ and $z(\sigma,x)$ are nonlinear, which is a disadvantage, but they are local, and they are partially uncoupled. Equation (16) for y is independent of z. Although (17) depends on y, we can, in principle, solve (16) for y and substitute the solution into (17).

Finding the distributions now involves solving (16) for all σ and asymptotically small δ. It is convenient to restrict the explicit σ dependence to a single term, so define

$$\psi=y-i\sigma\mu\ln x \ .$$

Then

$$\delta\frac{d\psi}{dx}=x^{\mu}(1+e^{\psi})-(1+e^{-\psi})-\delta\frac{i\sigma\mu}{x} , \tag{19}$$

and the equilibrium value $\psi_0=-\mu\ln x$ is real for all σ. We follow the same procedure as for the population $n(x)$. An expression for ψ valid at high temperatures is obtained by expanding in powers of δ,

$$\psi=\sum_{k\geq 0}\delta^k\psi_k \ .$$

The first two terms in the outer solution are

$$\psi_0=-\mu\ln x ,$$

as expected, and

$$\psi_1=-\frac{\mu}{x}\frac{1-i\sigma}{1+x^{\mu}} . \tag{20}$$

Since

$$n=\{1+\exp[\psi(\sigma)]\}^{-1}|_{\sigma=0} ,$$

we see that (20) is consistent with (9), also as expected.

For the inner, low-temperature expansion, let $X\equiv x/x_0$ and $\Psi(X)\equiv\psi(x)$ in (19). Letting $x_0=\delta$ is again appropriate, yielding

$$\frac{d\Psi}{dX}=x_0^{\mu}X^{\mu}(1+e^{\Psi})-(1+e^{-\Psi})-\frac{i\sigma\mu}{X} . \tag{21}$$

Expanding Ψ in powers of x_0^{μ} appears to be the obvious tactic, but unfortunately it produces nonsensical results for $\sigma=0$. The $\sigma=0$ solution is known from the inner expression for n:

$$\begin{aligned}\Psi(\sigma=0, X)&=\ln[1-n(x)]-\ln n(x)\\ &\approx -n(x)-\ln n(x)\\ &\approx -x_0^{\mu}e^{X}\Gamma(1+\mu,X)-\ln x_0^{\mu}-X\\ &\quad -\ln\Gamma(1+\mu,X)\\ &=O(x_0^{\mu})+O(\ln x_0^{\mu})+O(1)\ .\end{aligned}$$

Therefore we must expand Ψ in powers of x_0^{μ} and $\ln x_0^{\mu}$, and possibly all combinations thereof. It is sufficient, fortunately, to write

$$\Psi(x)=\sum_{k\geq 0} x_0^{\mu k}[\Psi_k(X)+\Phi_k(X)\ln x_0^{\mu}]\ .$$

Then

$$e^{\pm\Psi}=e^{\pm\Psi_0}x_0^{\pm\mu\Phi_0}\{1\pm x_0^{\mu}[\Psi_1+\ln(x_0^{\mu})\Phi_1] + O(x_0^{2\mu})+O(x_0^{2\mu}\ln x_0^{\mu})\}\ .$$

There will be negative powers of x_0 on the right-hand side of (21) unless we set $\Phi_0=-1$. Collecting terms of equal order in (21) we find, to lowest order,

$$\frac{d\Psi_0}{dX}=X^{\mu}e^{\Psi_0}-1-\frac{i\sigma\mu}{X}\ ,$$

the solution of which is

$$\Psi_0(X)=-X-\ln[X^{i\sigma\mu}\Gamma(1+\mu(1-i\sigma),X)]\ . \tag{22}$$

An arbitrary function $F(\sigma)$ could be added to the gamma function, but the inner and outer solutions match, to lowest order, only for $F=0$. The uniformly valid expression turns out to be identical to the inner solution (22).

Unraveling the changes of variables, we find[11]

$$\frac{\tilde{\rho}_{\uparrow}(\sigma,x)}{\tilde{\rho}_{\downarrow}(\sigma,x)}=x_0^{\mu(1-i\sigma)}e^{x/x_0}\Gamma(1+\mu(1-i\sigma),x/x_0) \tag{23}$$

and

$$\ln[\tilde{\rho}_{\downarrow}(\sigma,x)\tilde{\rho}_{\uparrow}(\sigma,x)]=f(\sigma)+\frac{1}{x_0}\int_x^1 dz\left[1+z^{\mu}+z^{\mu(1-i\sigma)}\frac{\tilde{\rho}_{\downarrow}(\sigma,z)}{\tilde{\rho}_{\uparrow}(\sigma,z)}-z^{i\sigma\mu}\frac{\tilde{\rho}_{\uparrow}(\sigma,z)}{\tilde{\rho}_{\downarrow}(\sigma,z)}\right]\ . \tag{24}$$

The function $f(\sigma)$ depends on the initial high-temperature distribution, and is $2(i\sigma-1)\ln 2$ for the initial condition (7).

The dotted line in Fig. 5 is the distribution derived from Eqs. (23) and (24). For both the asymptotic curve and the Monte Carlo calculation, the asymmetry $\mu=0.5$ and the cooling rate $\delta=0.01$. Considering that 0.01 is not very small, the agreement is remarkable. For physical cooling rates ($\delta\lesssim 10^{-12}$) the agreement should be excellent.

The entropy distribution itself is a probe of the glassy dynamics, but it is useful to relate it to other properties, such as the freezing temperature, T^*. We do this to demonstrate that the freezing temperature derived from the distribution is consistent with more intuitive definitions. Using the asymptotic form of the entropy distribution by combining Eqs. (18) and (23) gives

$$\frac{V}{T^*}=-\ln x_0-\frac{\partial}{\partial\mu}\ln\Gamma(1+\mu)\ . \tag{25}$$

We can also equate the freezing temperature with the width of the inner region, $\exp(-V/T^*)=x_0$, implying that $V/T^*=-\ln x_0$. The temperature at which the rate of change of the equilibrium population equals the transition rate is given by (5), which implies $V/T^*\approx -\ln\delta\mu$. For large μ and small δ, these three expressions are all equivalent, especially given the uncertainty in the definition of T^*. When μ is small, the expressions differ, but because the two wells of the TLS are nearly identical in this case, the temperature at which the TLS falls out of equilibrium is even less well defined.

Yet another estimate of T^* is the temperature at which the equilibrium population equals the asymptotically calculated residual population,

$$n_0(T^*)=x_0^{\mu}\Gamma(1+\mu)-\frac{x_0^{2\mu}}{1+x_0^{\mu}}\ . \tag{26}$$

Expressions (25) and (26) are plotted in Fig. 6 along with the distance between the peaks in the Monte Carlo TLS simulations. All the expressions agree, providing a check on the asymptotic analysis.

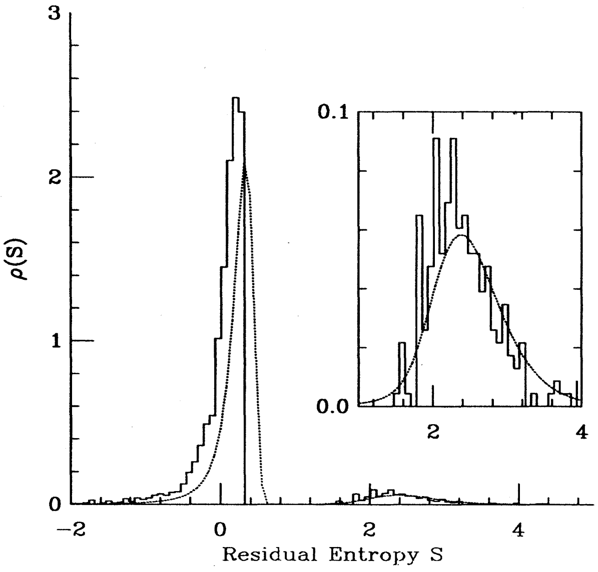

FIG. 5. Entropy distribution for a TLS with asymmetry $\mu=0.5$, cooled to $T=0$ at a cooling rate $\delta=0.01$. The solid line is the result of a Monte Carlo simulation, while the dotted line is the asymptotic expression (23) and (24).

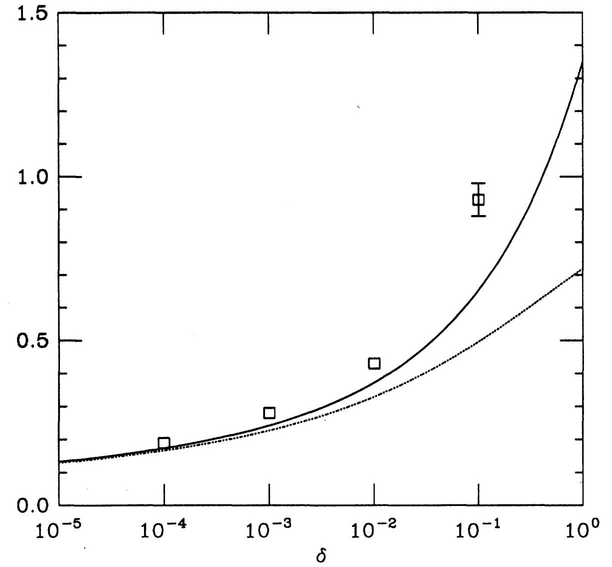

FIG. 6. "Freezing" temperature T^* for a TLS as a function of dimensionless cooling rate δ. The solid curve is predicted from the distance between the peaks in the entropy distribution [Eq. (25)], the dotted curve is predicted from the residual population [Eq. (26)], and the points are extracted from the entropy distributions measured by Monte Carlo simulation of a TLS.

V. CONCLUSIONS

We have shown two things: The energy and the entropy distribution for a simple model glass can be calculated in the limit of slow cooling, without making any assumptions about equilibrium, and information (in the form of T^*, in this case) can be extracted from the entropy distribution. The technique, here applied to a simple glass, should be applicable to more complicated models. In a follow-up paper,[6] we will present numerical studies of the entropy distribution of the TLS and spin glasses.

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APPENDIX: LINEAR COOLING

Given an arbitrary cooling or heating schedule $T(t)$, the master Eqs. (4) for the population, in terms of x and μ, reads

$$\left[-\frac{\dot{T}(x)(\ln x)^2}{\Gamma_0 V}\right]\frac{dn}{dx}=-x^{\mu}+(1+x^{\mu})n(x)\,, \qquad (27)$$

where $\dot{T}(x)=dT(x(t))/dt$. For the "simple" cooling rate used in the text, $T(t)=T_0/(1+Rt)$, the term in braces on the left-hand side of (27) is constant, and set equal to δ. For linear cooling, $T(t)=T_0-rt$, we define $\delta=r/\Gamma_0 V$, and the master equation is

$$\delta\frac{dn}{dt}=\frac{1}{(\ln x)^2}[-x^{\mu}+(1+x^{\mu})n(x)]\,. \qquad (28)$$

The outer expansion proceeds as before: Expanding $n(x)$ in powers of δ, we find

$$n(x)=\frac{x^{\mu}}{1+x^{\mu}}\left[1+\delta\mu\frac{(\ln x)^2}{x(1+x^{\mu})^2}+O(\delta^2)\right]\,, \qquad (29)$$

which differs from the equivalent expression (9) for the simple rate only in the factor of $(\ln x)^2$ in the first-order term. This factor will not affect the asymptotic match, since we matched the inner and outer formulas only to zeroth order.

Rewriting the master equation in terms of the inner variables, $X=x/x_0$ and $N(X)=x_0^{-\mu}n(x)$, now yields

$$\frac{\delta(\ln x_0)^2}{x_0}\frac{dN}{dX}=\left[1+\frac{\ln X}{\ln x_0}\right]^{-2}[-X^{\mu}+(1+x_0^{\mu}X^{\mu})N(X)]\,. \qquad (30)$$

As before, we identify the width of the inner region by requiring that the coefficient of the derivative not be small. Hence

$$x_0=\delta(\ln x_0)^2\,.$$

Since $X=O(1)$ in the inner region, and $x_0 \ll 1$, the term in braces on the right-hand side of (30) is unity, to order $O(1/\ln x_0)$. Therefore, neglecting the term in braces, the inner solutions for the linear simple cooling schedules will be the same, except for the differences in x_0. The uniform solution, matched to zeroth order, will therefore be identical to (13).

Huse and Fisher[9] found

$$n(0)=\delta^{\mu}\left[\ln\frac{\delta}{\mu}\right]^{2\mu}\Gamma(1+\mu)-\frac{\delta^{2\mu}}{1+\delta^{\mu}}\,, \qquad (31)$$

which agrees asymptotically with our result as $\delta\rightarrow 0$. For unknown reasons, our expression is slightly better than theirs at larger cooling rates.

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[7] There is no paradox here, although the system is in a definite state and the entropy is not zero. We are talking about a single TLS, and the entropy measured by integrating the heat flow, not an ensemble of TLS's, nor the statistical entropy.

[8] Given this intial distribution, the equilibrium distribution at finite temperature consists of two delta functions of weight n_0 and $1-n_0$ centered at $S_{\uparrow}^{0}=S_0+(1-n_0)\beta\varepsilon$ and $S_{\downarrow}^{0}=S_0-n_0\beta\varepsilon$, respectively, where $S_0=\ln(1+e^{-\beta\varepsilon})+n_0\beta\varepsilon$ is the equilibrium entropy.

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[11] The up and down arrows are reversed in this equation [Eq. (5)] in Ref. 5.

[12] As mentioned in the text, the cooling curve is discussed in Ref. 9. A figure similar to the heating curve may be found in Y. Bar-Yam, D. Adler, and J. D. Joannopoulos, *Proceedings of the International Symposium on Physics and Applications of Amorphous Semiconductors, Torino, 1987* edited by F. Demichelis (World Scientific, Singapore, 1988), p. 13.