

Memory Effects in the Two-level Model for Glasses.

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We study an ensemble of two-level systems interacting with a thermal bath. This is a well known model for glasses. The origin of memory effects in this model is a quasi-stationary but non-equilibrium state of a single two-level system, which is realized due to a finite-rate cooling and slow thermally activated relaxation. We show that single particle memory effects, such as negativity of the specific heat under reheating, vanish for a sufficiently disordered ensemble. In contrast, a disordered ensemble displays a collective memory effect [similar to the Kovacs effect], where non-equilibrium features of the ensemble are monitored via a macroscopic observable. An experimental realization of the effect can be used to further assess the consistency of the model.

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Introduction. Low temperature properties of glassy and amorphous materials have been an active field of research for more than 30 years [1]; see [2] for a review. Experiments have shown that many characteristics of amorphous materials, e.g., the temperature dependence of the specific heat, are universal but different from those of crystals. This evidence has captivated much interest in the attempt of producing a coherent theoretical picture [1, 2]. The ensemble of two-level systems (TLS) was one of the first models to fit the experiments. It successfully describes the low-temperature properties of glasses, e.g., the linear temperature dependence of the specific heat [2]. With time this model was improved to account for features of amorphous solids at higher temperatures [3, 4], and found applications in protein physics [5]. A drawback of the model is that there is an excessive freedom in choosing the distribution of the ensemble parameters.

In this letter we study the two-level model in the thermally activated regime, which is experimentally relevant if the temperature is neither too low (otherwise, one has to account for tunneling), nor too high (otherwise, the two-level picture breaks down) [3, 4]. For instance, such a model, with a gaussian distribution of disorder, explains the attenuation and velocity variation of acoustic waves in a range of temperature up to 300 K [6] and explains as well the fact that after cooling from temperature T_0 to T_1 , the rate of heat released dQ/dt is found to change from T_0^2/t in the tunnelling regime (e.g. $T_1 < T_0 < 3K$ for epoxy resin) to $T_1^{9/4}/t^a$ with $a < 1$, at higher temperature ($3K < T_1 < T_0 \lesssim 20K$ for epoxy resin) [7, 8].

Memory effects arise in the model when due to cooling down to low temperatures the thermal activation is impeded [9]. Thus the relaxation time increases to an extent that for realistic observation times each TLS is frozen in a non-equilibrium, quasi-stationary state, which—in contrast to its equilibrium analog—depends on the history of the relaxation [9]. Most visible effects of this non-equilibrium appear during the subsequent reheating, when due to thermal reactivation the single system spe-

cific heat becomes negative [10]. We shall show however that this single particle memory effects do not survive the averaging over a sufficiently disordered ensemble. In contrast, we propose to implement a memory effect, where *due* to the disorder in the ensemble, locally non-equilibrium features of the system are monitored via a macroscopic (disorder averaged) observable. This effect resembles the one implemented by Kovacs for glassy polymers [11], and since then studied actively [12]. The shape of the effect is sensitive to dynamic (relaxation) and static (disorder) features of the model.

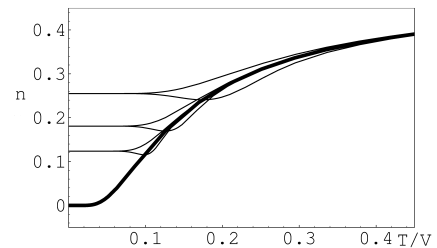


FIG. 1: Upper level occupation n vs. dimensionless temperature T/V for a single TLS with $\varepsilon/V=0.2$. Thick curve: n_{eq} . The pairs of normal curves refer to cooling (upper curves) and reheating (lower curves) with dimensionless rate (from top to bottom) $\sigma = 0.01, 0.001, 0.0001$.

The two-level model of glasses amounts to independent particles moving in an asymmetric double-well potential with ε and V being the energy difference between the wells and the barrier height, respectively [1, 2]. Each particle couples to a thermal bath. The positive variables ε and V change from one particle to another, so that to become observables the single-particle characteristics, such as energy or specific heat, should be averaged over the joint distribution $P(\varepsilon, V)$ to be specified later on. There are two regimes in the motion of the single system. *i)* The thermally activated regime is realized when the bath-particle coupling is sufficiently large. At each moment of time the particle is then effectively in one

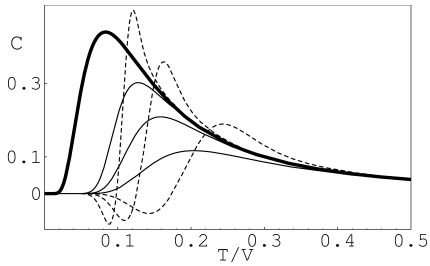


FIG. 2: Specific heat C for a single TLS vs. T/V with $\varepsilon/V = 0.2$. Thick curve: equilibrium C . Normal curves: C during protocol (3) with (from left to right) $\sigma = 0.0001, 0.001, 0.01$. Dashed curves: continuation of each cooling protocol by heating with the same σ (but opposite sign), starting at $T/V=10^{-4}$, when n has relaxed to its zero temperature value.

of the wells, making sudden jumps between them. The classical two-state approach is thus a good description of this regime. *ii*) For low temperatures and weak particle-bath couplings only the lowest two energy levels of the quantum double well Hamiltonian are relevant and the problem reduces to a quantum TLS coupled to a bath [2]. Here we study only the thermally activated regime. Let n and $1 - n$ be the probabilities for the particle to be in the higher and lower well, respectively. Within the thermally activated dynamics one has:

$$\dot{n} = \gamma_0 e^{-\beta(V+\varepsilon)}(1-n) - \gamma_0 e^{-\beta V} n, \quad (1)$$

where $e^{-\beta(V+\varepsilon)}$ and $e^{-\beta V}$ are the rates of the inter-well motion, $T = 1/\beta$ is the bath temperature, and where γ_0 is the attempt frequency. Eq. (1) is solved as

$$n_t = e^{-\frac{t}{\tau}}(n_0 - n_{eq}) + n_{eq}, \quad \tau = e^{\beta V} / [\gamma_0(1 + e^{-\beta\varepsilon})], \quad (2)$$

where τ is the relaxation time and $n_{eq}(\beta) = 1/(e^{\beta\varepsilon} + 1)$ the equilibrium value of n reached for $t \gg \tau$. At low temperatures the relaxation time τ becomes very large, since there is not enough energy for thermal activation. In this regime a freezing temperature T^* can be defined below which n is essentially frozen-in at $T = T^*$ [2, 9]. Note that besides TLS's there are other degrees of free-

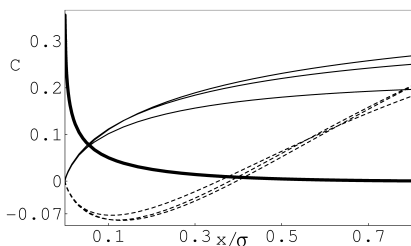


FIG. 3: Specific heat C versus $x/\sigma = \exp(-V/T)/\sigma$ for a single TLS with $\varepsilon/V = 0.2$. Thick curve: equilibrium C . Normal (dashed) curves: C got via cooling (reheating) protocol (3). From top to bottom: $\sigma = 1.5 \times 10^{-5}, 10^{-4}, 10^{-3}$.

dom (electronic, vibrational) whose contribution of the

total energy is not negligible in the thermally activated regime. However, the successful applications of TLSs for describing experiments indicate that at least for moderate temperatures the additional degrees of freedom decouple, and bring additive and equilibrated (since their relaxation is not impeded) contribution to the energy [3, 4, 6, 7, 9]. Thus they are not expected to be relevant for non-equilibrium features [2].

Cooling. Assume that the bath temperature is cooled according to the following non-linear protocol:

$$\beta_t \equiv 1/T_t = \beta_0 + \omega t \quad (3)$$

where $\omega > 0$ is the dimensional cooling rate. This protocol is reasonable for low T , since it satisfies the third law, not allowing cooling to $T = 0$ in a finite time. Expectedly, for a small rate ω and a high temperature T_t , n sticks to its equilibrium value $n_{eq}(\beta_t)$ while for lower T_t there will not be sufficient time to reach this value, since τ increases; see Fig. 1. We rewrite Eq. (1) as:

$$\sigma dn/dx = (x^\mu + 1)n(x) - x^\mu, \quad \sigma \equiv \omega V/\gamma_0, \quad \mu \equiv \varepsilon/V, \quad (4)$$

where the variable $x_t \equiv \exp(-\beta_t V)$ is introduced and σ is the dimensionless cooling rate. The solution of (4) is:

$$n(x) = n(x_0) \exp\left[\frac{x-x_0}{\sigma} + \frac{x^{\mu+1} - x_0^{\mu+1}}{\sigma(\mu+1)}\right] + \int_x^{x_0} dz \frac{z^\mu}{\sigma} \exp\left[\frac{x-z}{\sigma} + \frac{x^{\mu+1} - z^{\mu+1}}{\sigma(\mu+1)}\right], \quad (5)$$

where $x_0 \equiv \exp(-V/T_0)$. Note from (5) that the memory about the initial condition x_0 is eliminated for $x_0 \gg \sigma$. If this is satisfied and if σ is small, the integral in (5) is approximated as $[a(z) \equiv z^\mu, b(z) \equiv z + z^{\mu+1}/(\mu+1)]$:

$$\int_x^{x_0} dz a(z) e^{-\frac{b(z)}{\sigma}} \simeq \frac{\sigma a(x)}{b'(x)} e^{-b(x)/\sigma}. \quad (6)$$

Eqs. (5, 6) leads to the equilibrium value of n : $n(t) = x^\mu/(1+x^\mu) = n_{eq}(\beta(t))$. This, however, holds under neglect of terms $a'(x)(z-x)$ and $\frac{1}{2}b''(x)(z-x)^2$ in (6). Thus for the validity of the approximation we need: $a(x)b'(x) \gg \sigma a'(x)$ and $b''(x)\sigma \ll [b'(x)]^2$, which amounts to $\sigma\mu x^{\mu-1} \ll (1+x^\mu)^2$, and $\sigma\mu \ll x(1+x^\mu)$. For $\mu < 1$ and $x < 1$ we write the relevant conditions as

$$x \gg \sigma\mu \quad \text{or} \quad T \gg V/[-\ln(\sigma\mu)]. \quad (7)$$

For any finite $\sigma\mu$ this condition breaks down for low temperatures $x \rightarrow 0$. For these temperatures, $x \ll \sigma\mu$, we obtain a non-equilibrium, stationary (time-independent) value for n by putting in (5) $x = 0$. If in addition $x_0 \gg \sigma$, we put in (5) $x_0 = \infty$ and get for $\sigma^\mu \ll 1$:

$$n(0) = \int_0^\infty dz \frac{z^\mu}{\sigma} e^{-\frac{z}{\sigma} - \frac{z^{\mu+1}}{\sigma(\mu+1)}} = \sigma^\mu \Gamma(1+\mu) + o(\sigma^\mu). \quad (8)$$

Compared to n_{eq} , the non-equilibrium n in (8) depends on the dynamical quantities such as the attempt frequency γ_0 and the barrier height V : n is smaller for a slower cooling; see Fig. 1.

Note that some asymmetry $\varepsilon/V \equiv \mu \neq 0$ between the wells is crucial for $n(0) \neq n_{eq}$. For $\mu \rightarrow 0$ we get from the integral in (8) almost equilibrium result: $n(0) = 1/2 + \mu(\gamma_E + \ln \sigma/2)/4 + \mathcal{O}(\mu^2)$, where γ_E is Euler's gamma.

Specific heat—or the response of the energy εn on the temperature change—provides more visible effects of the memory on the relaxation history. Using (4) the equilibrium and the non-equilibrium specific heat are:

$$C_{eq} = \varepsilon dn_{eq}/dT = \mu^2 (\ln x)^2 x^\mu [1 + x^\mu]^{-2} \quad (9)$$

$$C = \varepsilon (dn/dt)(dt/dT) = \frac{\mu}{\sigma} x (\ln x)^2 [(x^\mu + 1)n(x) + x^\mu].$$

Since C_{eq} is zero both for high and low temperatures, it displays a maximum at some intermediate temperature; see Fig. 2. Under cooling from some high temperatures according to (3), the specific heat C_c shows signs of freezing: it is smaller than C_{eq} , saturates quicker to zero, and has a smaller maximum. Let us now terminate the cooling at some temperature T_l which is low enough so that the energy εn relaxed to its stationary value (8). Now heat up the bath using the same protocol (3) with $T_0 = T_l$ and $\omega < 0$, and the same dimensionless rate $|\sigma|$.

C_{eq} is the same for cooling and reheating. In contrast, the specific heat C_h under heating is seen to be negative for sufficiently small temperatures [10]. This is related to the decrease of the upper-level occupation n under reheating; see Fig. 1. Moreover, $C_h \approx -C_c$ at these temperatures: the system keeps memory of the cooling stage and still decreases its energy after thermal reactivation. Once C_h reaches its negative minimum, it quickly increases to the positive maximal value that can be larger than the maximum of C_{eq} : the reheating can bring in more thermal instability; see Fig. 2. For higher temperatures both C_c and C_h tend to C_{eq} .

The negativity of C_h shows that the quasi-stationary state of the TLS cannot be viewed as effective equilibrium, as far as the reheating is concerned. In order to make this result more clear, we note that in the slow limit, where one decreases $|\sigma|$ and simultaneously increases the time and T remains constant, we expect convergence to equilibrium. Indeed, the temperature region where C_h is negative, shrinks to zero as $\sim \ln(1/|\sigma|)$ [see (7)], but the magnitude of the negative minimal value of C_h in this region does not depend much on σ . This is seen upon plotting C_h versus $x/\sigma = \exp(-V/T)/\sigma$; see Fig. 3. However the negativity of C_h , and the very difference between C_h and C_c , is sensitive to the values ε and V of the single-system motion. This is seen, in particular, from the structure of the scaling variable x/σ in Fig. 3. We thus expect that upon averaging over the disorder the single-system memory effects gradually disappear, i.e., though each TLS remains non-equilibrium, C_h tends to

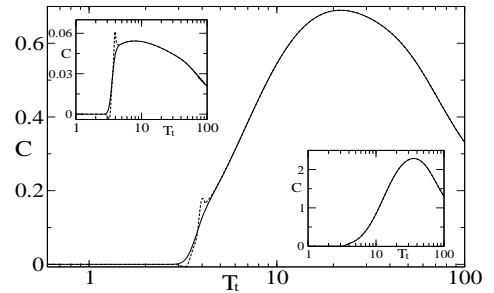


FIG. 4: Average sp. heat C vs. T_t in cooling from $T_0=100K$ (normal curve) to $T_l=1K$ and reheating (dashed curve), with cooling rate: $\omega=10^{-3}(Ks)^{-1}$ over the SPM distribution with: $V_m=100K$, $V_M=400K$, $\varepsilon_m=0K$ and $\varepsilon_M=5K$ (top left insert), $20K$ (main figure), $40K$ (bottom right insert). $\gamma_0 = 10^{12}s^{-1}$, as for experiments by A. Nittke *et al.* in [2].

C_c eliminating the difference between cooling and heating. The same holds for the energy εn . In order to illustrate this effect let us take the Soft Potential Model (SPM) approach, in which the probability $P(\varepsilon, V)$ is [3] proportional to $V^{-3/4}$ for $\varepsilon_m < \varepsilon < \varepsilon_M$, $V_m < V < V_M$ and zero elsewhere. The values of $\varepsilon_m, \varepsilon_M, V_m, V_M$ are found by fitting to experiments; see [3] for details. It is seen on Fig. 4, that the difference between the cooling and heating indeed disappears once the disorder is sufficiently strong. The same holds for other distributions of the disorder. We shall now discuss another method for displaying this non-equilibrium feature. In contrast to the above features which are essentially single-system and tend to disappear in the presence of disorder, the new method is based on the presence of an ensemble.

Temperature shift protocol. Motivated by Kovacs experiment [11], we perform the following protocol.

1. Consider an ensemble of non-interacting TLSs characterized by a distribution $P(\varepsilon, V)$. The ensemble is equilibrated at a given high temperature T_0 .

2. Between times $t = 0$ and t_c the bath is cooled down following (3). The cooling is terminated at a low temperature T_l so that the ensemble averaged energy $\langle \varepsilon n \rangle \equiv \int \varepsilon d\varepsilon dV P(\varepsilon, V) n(\varepsilon, V)$ reached a stationary value. This determines the final time t_c . Note that $\langle \varepsilon n \rangle$ is observable in experiments using, e.g., heat release measurements [2]. Now $\langle \varepsilon n \rangle$ equals its equilibrium value:

$$\langle \varepsilon n \rangle|_{t=t_c} = \langle \varepsilon [e^{\beta_f \varepsilon} + 1]^{-1} \rangle \equiv \langle \varepsilon n_{eq} \rangle. \quad (10)$$

This condition defines the temperature $T_f = 1/\beta_f$. If most of the TLSs in the ensemble happen to be described at $t = t_c$ by a single temperature, then this temperature will be close to T_f by definition. T_f turns out to be of the same order of the average freezing temperature $\langle T^* \rangle$.

3. We want to monitor via a macroscopic (i.e., ensemble-averaged) quantity to what extent the state of the ensemble reached at $t = t_c$ is really close to some internal equilibrium. To this end, the bath temperature

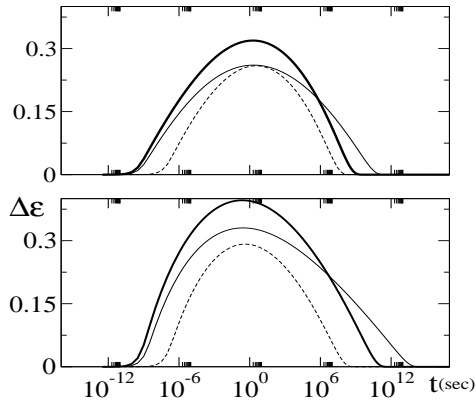


FIG. 5: $\Delta\varepsilon$ vs. time t for the disordered ensemble with flat distribution (top) of ε and V and with SPM distribution (bottom). The cooling protocol (3) is applied between $T_0=100K$ and $T_l=2K$, with $\omega=10^{-3} (Ks)^{-1}$. For all curves: $\varepsilon_m=0K, V_m=100K$ Thick curve: $\varepsilon_M=100K, V_M=800K$; $T_f=16.6K$ (top) and $15.12K$ (bottom). Normal curve: $\varepsilon_M=50K, V_M=800K$; $T_f = 15.3K$ (top) and $13.46K$ (bottom). Dashed curve: $\varepsilon_M=50K, V_M=400K$; $T_f = 8.8K$ (top) and $8.6K$ (bottom)

is suddenly switched to T_f , and the resulting evolution of $\langle\varepsilon n\rangle$ is monitored. Due to the sudden switching, the evolution is obtained averaging Eq. (2) at the bath temperature T_f , and with initial state (10):

$$\Delta\varepsilon \equiv \langle\varepsilon n_t\rangle - \langle\varepsilon n_{eq}\rangle = \langle\varepsilon e^{-\frac{t-t_c}{\tau}} (n - [e^{\beta_f\varepsilon} + 1]^{-1})\rangle. \quad (11)$$

It is seen from (11) that by our construction $\Delta\varepsilon$ should be zero both at $t = t_c$ and for a very large $t - t_c$. It will stay zero for all times $t > t_c$, if the state of (almost) each TLS in the ensemble is described by the same temperature (which need not be equal to that of the bath). Yet another case, where $\Delta\varepsilon$ is constant for $t > t_c$ is when there is no disorder in the ensemble. Thus, the change of $\Delta\varepsilon$ depends both on the disorder and on a non-equilibrium state at $t = t_c$. The behaviour of $\Delta\varepsilon$ for experimentally meaningful parameters is shown in Figs. 5. Since the change of $\Delta\varepsilon(t)$ is finite, a sizable fraction of the ensemble is at $t = t_c$ far from a local equilibrium. To gain more understanding, consider the simplest ensemble: an equal-weight mixture of two TLSs with parameters (ε_1, V_1) and (ε_2, V_2) . Eq. (11) implies

$$\Delta\varepsilon = (e^{-\frac{t-t_c}{\tau_1}} - e^{-\frac{t-t_c}{\tau_2}})[n(\varepsilon_1, V_1) - 1/(e^{\beta_f\varepsilon_1} + 1)]\varepsilon_1/2,$$

where $\tau_i = \exp(\beta_f V_i)/[\gamma_0(1 + \exp(-\beta_f\varepsilon_i))]$ for $i = 1, 2$ are the relaxation times (see (2)), $n(\varepsilon_1, V_1)$ is given by (8), and where the temperature β_f is defined as in (10) : $\sum_{i=1,2} \varepsilon_i n(\varepsilon_i, V_i) = \sum_{i=1,2} \varepsilon_i [e^{\beta_f\varepsilon_i} + 1]^{-1}$. For the considered simplest ensemble, $\Delta\varepsilon$ is *positive* for $t > t_c$. This is because the slower system—e.g., system 1, if $\tau_1 > \tau_2$ —has its non-equilibrium upper-level probability $n(\varepsilon_1, V_1)$ larger than the final equilibrium one $[e^{\beta_f\varepsilon_1} + 1]^{-1}$. In other words, the slower system is further

from the equilibrium. The behaviour of $\Delta\varepsilon(t)$ for an experimentally relevant disorder distributions is displayed in Figs. 5. The fact that $\Delta\varepsilon(t) \geq 0$ -which holds for all checked cases- implies the same explanation as above: the slow elements of the ensemble are further from equilibrium. Two important (and for the present effect general) facts seen in Fig. 5 is that the stronger disorder leads to *i)* larger value of T_f and *ii)* larger maximum of $\Delta\varepsilon$.

In conclusion, we studied memory effects in the two-level model for glasses. It is known [9, 10] that when a single TLS is cooled down to low temperatures, the relaxation time increases due to impeding of the thermal activation, and the TLS appears in a quasi-stationary, non-equilibrium state. In contrast to equilibrium, this state depends on the detailed features of the relaxation, such as the barrier height or the cooling rate. In reheating the non equilibrium nature of this state manifests itself via a negative specific heat [10].

We confirmed the latter results by showing that the negative magnitude of the reheating specific heat is almost insensitive to the decreasing of the cooling-reheating rate. Next we showed that the single-particle non-equilibrium (memory) effects disappear for a disordered ensemble. Our main result is that motivated by Kovacs experiments in [11], we designed a protocol which is able to reflect the non-equilibrium features of a disordered ensemble. The effect is sensitive to the details of the disorder and, if realized experimentally, it can assess the consistency of the model. We have also found two universal features of the effect: *i)* it is more visible for a stronger disorder and *ii)* its sign is determined by the fact that slower elements of the ensemble are further from equilibrium.

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