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Numerical study of ageing in coupled two-level systems

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ABSTRACT

We study a lattice model of coupled two-level systems by Monte Carlo simulation. We find that it has glassy behaviour (non-exponential relaxation, Vogel–Fulcher relaxation times and ageing) at low temperatures. We study, in particular, ageing of the susceptibility in the frequency domain and find that it differs from spin-glass behaviour in that it does not obey ωt_w scaling. Its qualitative features indicate that it may be a good model of ageing in structural glasses.

§ 1. INTRODUCTION

The glassy state is characterized by the presence of disorder, very slow relaxation and ageing, that is the non-equilibrium non-metastable regime which follows a quench, in which response and correlation functions depend on both frequency and *waiting time* t_w (the time elapsed since the end of the thermal treatment that prepared the glassy phase) (Struick 1978). These features are present in, among other systems, both spin and structural glasses, despite some important differences such as the absence of quenched disorder in structural glasses, or of a crystalline state in spin glasses. Indeed, the present understanding of structural glasses has benefited from theoretical progress in the study of spin systems, following the replica solution (Mézard *et al*. 1987) of the Sherrington–Kirkpatrick (1975) model. Central to the relevance of spin models to structural glasses is their ageing behaviour (Bouchaud *et al*. 1998). At the mean-field level it turns out (Bouchaud *et al*. 1998) that models exhibiting so-called one-step replica symmetry breaking (1-RSB), like the p spin, show a behaviour analogous to structural glasses in two ways. Firstly, there is a dynamic critical temperature T_c (which corresponds to the mode-coupling temperature) below which, in the thermodynamic limit, the system never equilibrates. Equilibrium properties remain, however, analytic at T_c, and the phase transition to a state with broken replica symmetry happens at a temperature $T_s < T_c$. This is in parallel to the purely dynamic transition normally observed experimentally in structural glasses around T_g, although here activated processes do eventually bring the system to equilibrium. Secondly, 1-RSB models have only two time scales (sometimes called time sectors), which implies that fluctuation–dissipation theorem (FDT) violations (Cugliandolo and Kurchan 1993, 1994, 1995) can be described with only one effective temperature. This is the same behaviour found in numerical studies of

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fluctuation–dissipation relations in soft sphere (Parisi 1997, 1998) and Lennard-Jones (Barrat and Kob 1999, Di Leonardo *et al.* 2000) glasses. The success of this analogy despite the approximation involved in neglecting activated processes has prompted a recent study (Ricci-Tersenghi *et al.* 2000) which found the same scenario in a short-range spin model (the frustrated Ising lattice gas).

However, recent experiments pointed to some qualitative differences in the ageing of spin and structural glasses. On the one hand, there are measurements of the imaginary susceptibility (out-of-phase response to an ac field) $\chi''(\omega, t_w)$. In the case of spin glasses, it has been found experimentally (Vincent *et al.* 1997, Hammann *et al.* 2000) that $\chi''(\omega, t_w) - \chi_0(\omega)$ (where $\chi_0''(\omega)$ is the equilibrium value) is a function only of the scaling variable ωt_w. This is also true for the p spin (Bouchaud *et al.* 1998) and Edwards–Anderson (Picco *et al.* 2001) models. In structural glasses, however, this scaling is not valid, as has been demonstrated by Leheny and Nagel (1998) in a careful study of the ageing of dielectric susceptibility in glycerol. FDT violations seem to indicate another difference. While in spin-glass models (mean field (Cugliandolo and Kurchan 1993, 1994) and Edwards–Anderson (Franz and Rieger 1995, Marinari *et al.* 1998)) violations are found for waiting times such that ωt_w is at most a few times unity, a recent experiment (Grigera and Israeloff 1999) on glycerol found violations that lasted up to $\omega t_w \approx 10^5$.

In this paper we study a lattice model based on two-level systems (TLSs). Tunnelling TLSs have been invoked before (Anderson *et al.* 1972, Philips 1972) to explain thermal properties of glasses at low temperatures, the central hypothesis being that in any glass system there should be a certain number of atoms (or groups of atoms) which can sit in two equilibrium positions. Energy landscape considerations (Angelani *et al.* 2000, Broderix *et al.* 2000) also lead us to expect these kinds of state, and that they be relevant near T_g. In fact, switching between two to four levels has been directly observed near T_g (Vidal-Russel and Israeloff 2000). At these temperatures, thermal activation, instead of tunnelling, would be the relevant mechanism of the switching. However, ageing cannot be explained by non-interacting TLSs, nor can certain low-temperature experiments (Salvino *et al.* 1994). The need for coupling between slow and fast degrees of freedom was also suggested by FDT violations (Grigera and Israeloff 1999).

We propose a quenched-disorder short-range model (§ 2) consisting of a TLS with a simple coupling that introduces energy transfer between neighbouring TLSs upon switching. We find (§ 3) ageing in the susceptibility that does not obey ωt_w scaling. In addition the model shows interesting behaviour at the site level, which we compare with recent experiments. This model could serve as an idealized system to study ageing in structural glasses.

§ 2. Details of the model and simulation

The model consists of TLSs (whose degree of freedom is described by the variables $S_i = \pm\frac{1}{2}$), sitting in a lattice and coupled with the Hamiltonian

$$H = \sum_i E_i, \tag{1}$$

$$E_i = E_i^0 + f_i(S_i + \tfrac{1}{2})\Delta_i - P_i h, \tag{2}$$

where the sum is over all the lattice sites, h is an external field and $P_i = k_i S_i$ is the site dipolar moment. k_i is taken to be $+1$ or -1 with equal probabilities. Δ_i is the energy

difference between the wells of the TLS at site i, which we choose randomly from a distribution uniform in the interval $[0, \Delta_{\max}]$, as has been done before (Philips 1972, Anderson *et al.* 1972). The coupling between TLSs comes in through the factor f_i, which is defined as

$$f_i = 2^z \prod_{j \in \mathrm{nn}(i)} S_j, \tag{3}$$

where z is the lattice coordination number and $\mathrm{nn}(i)$ is the set of nearest neighbours of site i. f_i can take the values $+1$ or -1 depending on the configuration of the neighbouring sites. Thus, when one of the neighbours switches, the effect on site i is that the relative height of the wells is reversed (i.e. the excited state becomes the ground state and vice versa).

For the dynamics, it is assumed that between the states $S_i = -\frac{1}{2}$ and $S_i = +\frac{1}{2}$ there is a potential barrier B_i which is taken in the interval $[B_{\min}, B_{\max}]$. Unless stated otherwise, runs were carried out with a peaked barrier distribution: the distribution was taken flat in $[B_{\min}, B_p]$ and $[B_p, B_{\max}]$, but four times larger in the latter interval.

We have studied this model numerically by Monte Carlo simulation on the square lattice ($z = 4$), setting $E_i^0 = 0$, $\Delta_{\max} = 4$, $B_{\min} = 5$, $B_p = 18$ and $B_{\max} = 20$. We used a standard single-site Metropolis algorithm. So that the detailed balance condition

$$p_{\mathrm{a}\to\mathrm{b}} \exp(-\beta E_{\mathrm{a}}) = p_{\mathrm{b}\to\mathrm{a}} \exp(-\beta E_{\mathrm{b}}) \tag{4}$$

is obeyed, we choose the transition probabilities as

$$p(S_i = -\tfrac{1}{2} \to S_i = \tfrac{1}{2}) = \exp\{-\beta[\tilde{B}_i - H(S_i = -\tfrac{1}{2})]\}, \tag{5}$$

$$p(S_i = \tfrac{1}{2} \to S_i = -\tfrac{1}{2}) = \exp\{-\beta[\tilde{B}_i - H(S_i = \tfrac{1}{2})]\}, \tag{6}$$

where $\tilde{B}$ is defined as

$$\tilde{B}_i = \max\{H(S_i = -\tfrac{1}{2}) - E_i^0 + B_i, H(S_i = \tfrac{1}{2}) - E_i^0 - f_i \Delta_i + B_i\} \tag{7}$$

To understand the last expression, take the case of a switch from $S_i = -\frac{1}{2}$ to $S_i = \frac{1}{2}$. If the switch lowers (or leaves unchanged) the energy of all its nearest neighbours combined (i.e. $H(S_i = -\frac{1}{2}) - E_i^0 \geqslant H(S_i = \frac{1}{2}) - E_i^0 - f_i \Delta_i$), the transition probability is just $\exp[-\beta(B_i - E_i^0)]$. However, if the switch results in an increase δE in the neighbours' energy, then the probability is $\exp[-\beta(B_i - E_i^0 + \delta E)]$. In other words, we are assuming that the switching involves jumping to an intermediate state (the barrier), rearranging the neighbours' levels (with a possible energy increase) and finally jumping to the final state. Of course the actual process can be more complex, but this is a necessary simplification if we want to utilize Hamiltonian (1).

Simulations were made on an $L \times L$ ($L = 32$ or 64) lattice with periodic boundary conditions. All results reported are averages over 8–26 different initial conditions and realizations of the disorder and thermal bath. Three kinds of run were carried out: quenches with an ac field, quenches without a field, and equilibrium runs with a dc field. The quenches were performed starting from infinite temperature (random configuration) and suddenly setting it to a final value of $T = 10$, 5, 3.3, 2.5, 2 and 1.5. In the first four cases, the runs lasted more than 100 equilibrium relaxation times (as determined *a posteriori*). The final state of these runs was used as the starting state for the equilibrium runs, in which a constant field h was applied and evolution of the

average polarization per spin was recorded. It was verified that the field was weak enough for the response to be in the linear regime.

The quenches to $T = 2$ and 1.5 were also carried out with an applied sinusoidal field $h(t) = h_0 \sin(\omega t)$. The time-dependent polarization $P(t)$ was recorded and the ac susceptibility was then obtained through

$$\chi'(\omega, t_w) = \frac{2}{h_0} \int_{t_w - Q/2}^{t_w + Q/2} P(t) \sin(\omega t)\, dt,$$
$$\chi''(\omega, t_w) = -\frac{2}{h_0} \int_{t_w - Q/2}^{t_w + Q/2} P(t) \sin\left(\omega t + \frac{\pi}{2}\right) dt, \tag{8}$$

where the integrals are over at least ten periods of the field ($Q = 20\pi/\omega$). This is very much like when the ac susceptibility is measured experimentally with a lock-in amplifier.

§ 3. Results

3.1. *Energy and polarization relaxation*

We first look at the energy approach to equilibrium after a quench without external field. When quenched to $T = 10$ and $T = 5$ a fast decay is observed that can be well fitted by a stretched exponential $E_0 + A \exp[-(x/\tau)^{\beta}]$ (figure 1). For quenches to $T = 3.3$ and below, however, a stretched exponential is no longer a good fitting function. Instead, there is a short-time regime which could be described by a power law (although $\log t$ is also possible), followed by a stretched-exponential regime at longer times (figure 1). A similar two-regime decay was observed in simu-

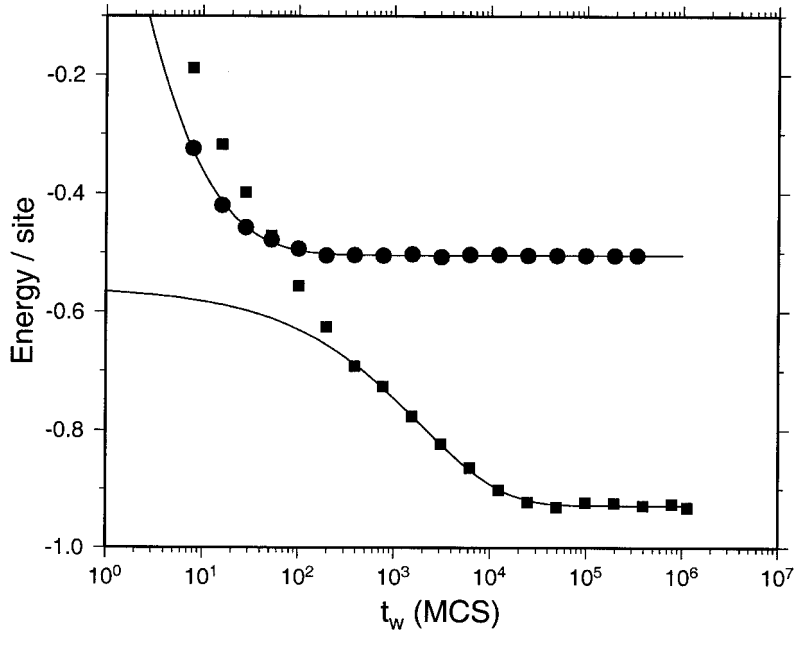

Figure 1. Energy per site versus waiting time (in Monte Carlo steps (MCS)) after quenches to $T = 5$ (●) and $T = 2.5$ (■): (——), are stretched-exponential fits.

lations of a soft-sphere binary mixture (Coluzzi and Parisi 1998). There is an initial regime with mean-field-like behaviour, which crosses over to a stretched-exponential decay when activated processes begin to dominate the dynamics.

The temperature at which the two-regime energy relaxation starts to be evident marks also the onset of stretched-exponential relaxation in equilibrium. We show the equilibrium relaxation of the polarization $P(t)$ after a dc field is applied at $t = 0$ in figure 2. At $T = 10$ and 5, the relaxation is simple exponential. At $T = 3.3$ and 2.5, however, it becomes stretched exponential with β around 0.6. By fitting these curves, we obtain a relaxation time which is shown in figure 3 as a function of inverse temperature in an Arrhenius plot. The temperature dependence is non-Arrhenius, and can be reasonably fitted with a Vogel–Fulcher form $\tau = A \exp[B/(T - T_0)]$ with $T_0 \approx 1.3$. Essentially the same result is obtained if the relaxation time is defined as the τ such that $P(\tau) = xP(\infty)$, with $x = \frac{1}{2}$ or $x = 1 - 1/e$.

3.2. *Susceptibility ageing*

Next we study ageing in the ac susceptibility $\chi(\omega, t_w)$. This is computed by applying a sinusoidal field at several frequencies after quenching and using equations 8. At the two lowest temperatures studied ($T = 2$ and $T = 1.5$), both the real and the imaginary parts show a strong t_w dependence (figure 4). As in the spin-glass case (Hammann *et al.* 2000), a power law fits the decay well, although a stretched exponential cannot be completely ruled out.

In figure 5 we plot the imaginary part of the susceptibility against the spin-glass scaling variable ωt_w. The scaling plots are obtained by subtracting a constant $K(\omega)$ from the susceptibility. This constant should be the equilibrium susceptibility.

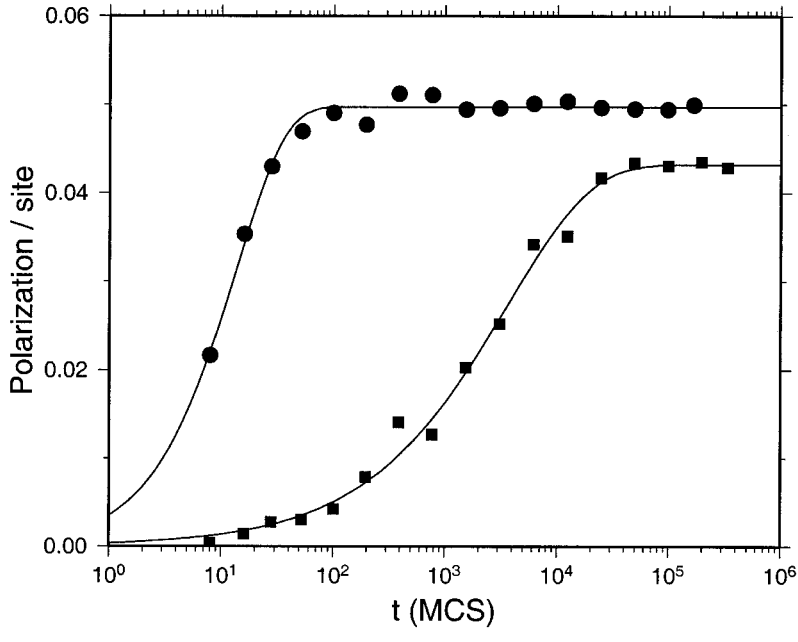

Figure 2. Polarization relaxation in equilibrium: (●), $T = 5$; (■), $T = 2.5$; (——), exponential ($T = 5$) and stretched-exponential ($T = 2.5$) fits.

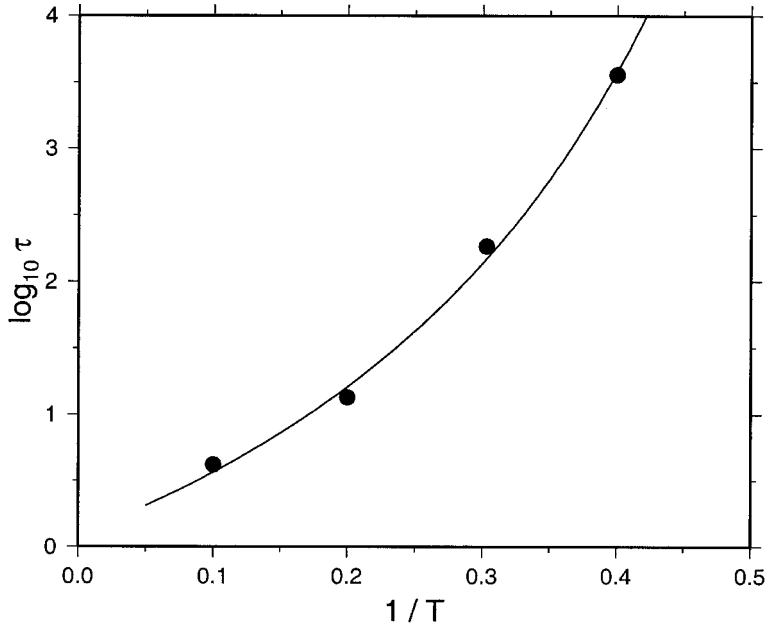

Figure 3. Equilibrium relaxation time versus inverse temperature.

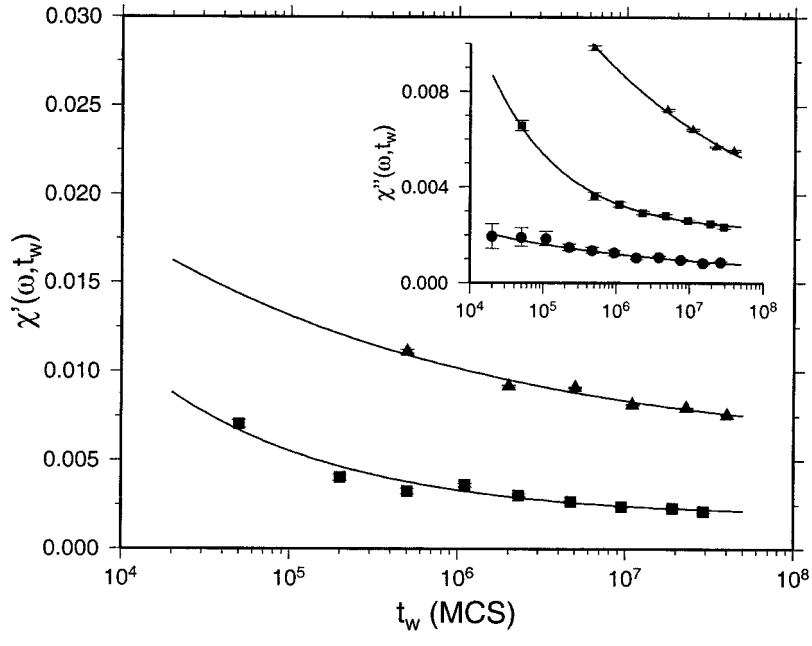

Figure 4. Ageing of the real (main figure) and imaginary (inset) parts of the ac susceptibility after a quench to $T = 1.5$: (●), $\omega = 2\pi 10^{-3}$; (■), $\omega = 2\pi 10^{-4}$; (▲), $\omega = 2\pi 10^{-5}$; (——), power-law fits.

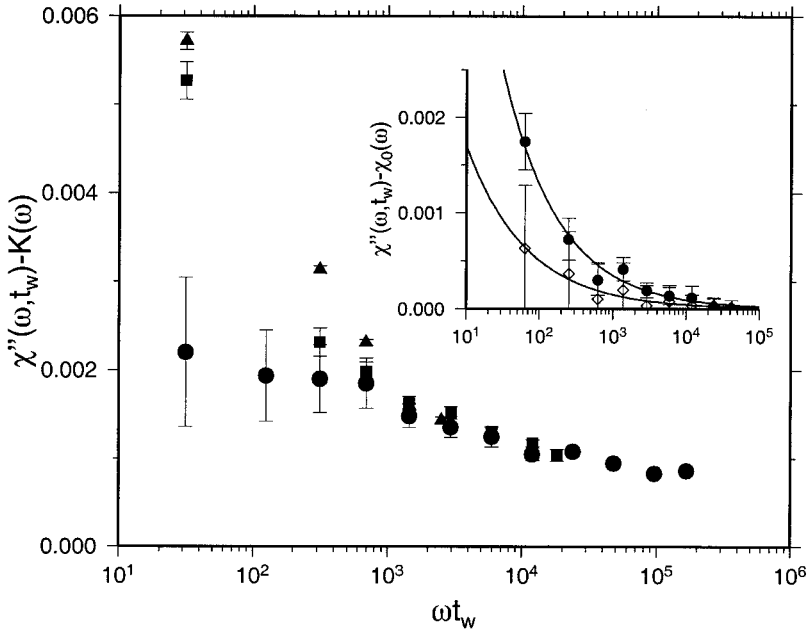

Figure 5. Ageing imaginary susceptibility plotted against the spin-glass scaling variable ωt_w for $T = 1.5$ and $T = 2$ (inset): (●), $\omega = 2\pi 10^{-3}$; (■), $\omega = 2\pi 10^{-4}$; (▲), $\omega = 2\pi 10^{-5}$; (◇), $\omega = 2\pi 10^{-2}$.

However, since the equilibrium value is not usually measurable, scaling of experimental data is achieved by subtracting an arbitrary amount, which gives the best scaling (Vincent *et al.* 1997). The same procedure was followed in recent simulation of the Edwards–Anderson model (Picco *et al.* 2001). Here we have subtracted the asymptotic value of the power-law fits $\chi_0''(\omega)$ in the cases where the simulation data reach values very close to it. Otherwise, we used an arbitrary constant. This was done with the aim of better comparison with the glycerol experiments (Leheny and Nagel 1998), where the equilibrium value was measured sufficiently close to T_g.

The quench to $T = 1.5$ was repeated for a system with a flat distribution of barriers (figure 6). In both cases it is clear that ωt_w scaling fails. However, in the flat-barrier case, the curves for low frequencies seem to reach equilibrium for values of ωt_w lower than those of higher frequencies. This is what is found in the experiments (see discussion below).

3.3. *Individual sites*

Finally, it is interesting to look at the behaviour of individual sites in equilibrium. We choose a site and record the time that it spends in a given state before switching. The distribution of this time, which we call the distribution of state duration, contains interesting information. For an isolated TLS, the distribution would be exponential: $N(t) = N_0 \exp(-t/\tau)$. This is not the case for the present model, as can be seen in figure 7. Instead, the distribution is double exponential ($N(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$) at $T = 2.5$ and stretched exponential with $\beta = 0.727$ at $T = 5$.

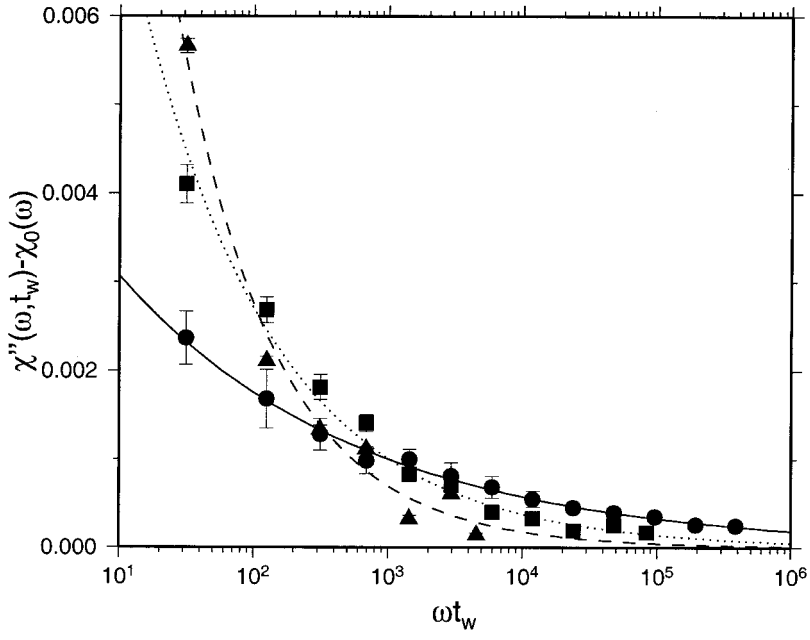

Figure 6. Ageing imaginary susceptibility of a system with a flat distribution of barriers quenched to $T = 1.5$, where $\chi_0(\omega)$ is the asymptotic value obtained from the power-law fits (——, ……, - - -): (●), $\omega = 2\pi 10^{-3}$; (■), $\omega = 2\pi 10^{-4}$; (▲), $\omega = 2\pi 10^{-5}$.

In a recent experiment (Vidal-Russell and Israeloff 2000), spontaneous switching of nanometre-scale clusters between two or more configurations with different dipole moments was observed in poly(vinyl acetate) slightly below T_g. This random telegraph noise was analysed by computing the distribution of state durations, and it was found that they are stretched exponential. Further, distributions obtained by averaging over short times were found to be simple exponential, and hence it was concluded that the stretching is due to modulation of the relaxation times.

These clusters could be thought of as represented by an individual lattice site of the present model. In fact, figure 7 arises, as in the experiment, from changes in the relaxation time of the site. This can be seen from equation (7), which shows how the effective barrier $\tilde{B}_i$ (and hence the relaxation time) changes upon flipping of the neighbouring sites. To understand why only two relaxation times are visible at $T = 2.5$, we should remark that in this case the average is made over approximately 5700 bulk relaxation times, while at $T = 5$ the value is about 302 000. It is also possible that, since $\tilde{B}_i$ can only take a finite number of values, the different relaxation times spread too much at lower temperatures, making a stretched exponential a poor approximation.

§4. Discussion and conclusions

The results on the energy and polarization relaxation show that the model of coupled two-level systems (CTLSs) that we have described here has glassy behaviour when quenched to low temperatures. The energy has a two-regime relaxation (first power law and then stretched exponential), and the polarization (in equilibrium) relaxes non-exponentially. The equilibrium relaxation time grows more rapidly

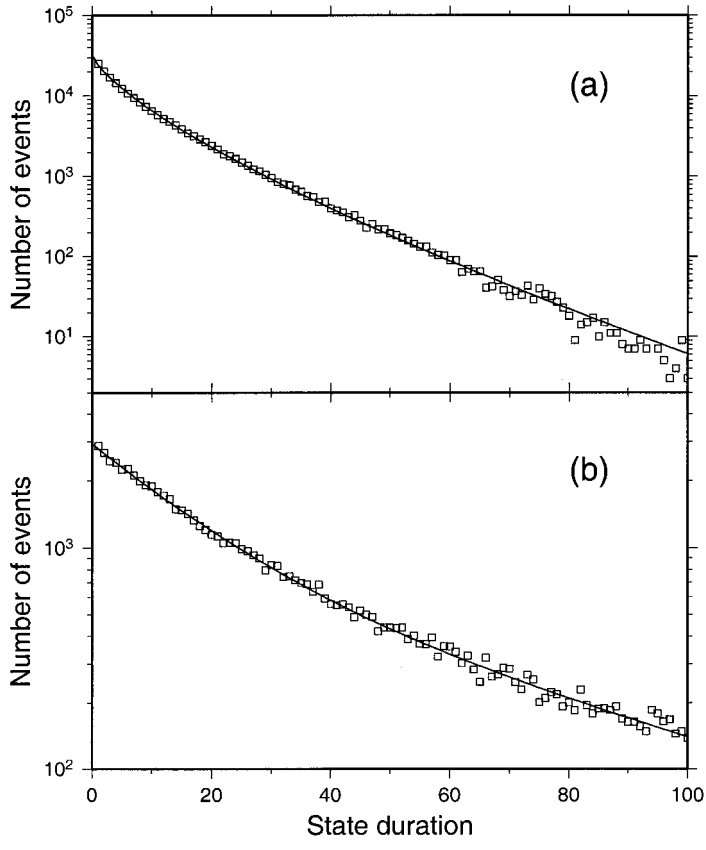

Figure 7. Distribution of state duration for one site at (*a*) $T = 5$ and (*b*) $T = 2.5$. The lines are fits of (*a*) stretched exponential with $\beta = 0.727$ and (*b*) a double exponential with relaxation times $\tau_1 = 56$ and $\tau_2 = 16$.

than the Arrhenius law as the temperature is lowered (the present results can be well fitted by a Vogel–Fulcher form). Finally, the ac susceptibility shows clear ageing, another fundamental ingredient of glassy phenomenology.

This study of the CTLS was made, looking for a lattice model that would age like structural glass. Experiments on glycerol (Leheny and Nagel 1998) show that, during ageing,

(i) the susceptibility at a fixed frequency decays following a stretched-exponential law and
(ii) it does not scale with ωt_w and, moreover, reaches the equilibrium value at values of ωt_w which are smaller for lower frequencies (Leheny and Nagel 1998, figure 13).

Another manifestation of this rather surprising point (ii) is the fact that the relaxation time of the stretched-exponential fits increases with increasing frequency (Leheny and Nagel 1998, figure 10). This contrasts with the findings in spin glasses (Vincent *et al.* 1997, Hammann *et al.* 2000) which show that susceptibility in these systems decays as a power law and obeys ωt_w scaling.

The present results clearly show that susceptibility ageing in CTLSs does not obey ωt_w scaling. The decay law could be reasonably fitted with a power law, but the current data are not enough to distinguish this from a stretched exponential. A subtler point is whether point (ii) above is reproduced by the model. This seems to be true in the flat-barrier case (figure 6).

Finally, studies of the dynamics at the site level may also be useful, in view of the experimental observation (Vidal-Russell and Israeloff 2000) of two- to four-level switching near T_g.

In summary, the results presented here, although not definitive, suggest that the CTLS is a good candidate to model ageing in structural glasses and warrants further investigation. In particular, studying the fluctuation-dissipation ratio during ageing would be interesting.

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