

## THE NATURE OF GLASS DYNAMICS: THERMAL REVERSIBILITY OF SPECTRAL DIFFUSION IN A LOW TEMPERATURE GLASS

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Temperature cycling optical hole-burning experiments on cresyl violet in ethanol glass are reported. At 1.3 K a hole is burned and measured. The temperature is then raised to 2.1 K; the hole is measured. The temperature is returned to 1.3 K, and the hole is again measured. The hole is observed to be narrow at 1.3 K, broader at 2.1 K, and then narrow again when the temperature is returned to 1.3 K. Using the time-dependent hole widths and photon echo data at the two temperatures, the results can be accounted for quantitatively using the tunneling two-level system model of glasses. Models of glasses, which involve processes such as spatial diffusion of defects, cannot account for the data.

### 1. Introduction

Glasses, unlike crystals, do not have a fixed, time-independent structure. They are inherently non-equilibrium systems with a vast variety of local structures. The structures evolve under the influence of thermally driven mechanical perturbations. Structural changes have been invoked to explain the anomalous heat capacities of glasses [1,2], thermal conductivity [1,2], phonon echoes [3], as well as a variety of optical experiments including photon echoes [4,5] and hole-burning experiments [5,6].

The results of all the experiments discussed above have been analyzed in some manner using the tunneling two-level system (TLS) model of glass dynamics [1,2]. In the TLS model, it is assumed that a local structural change in the glass can be described as a transition between two halves a double well potential, each half representing a particular local structure. A change in the local structure corresponds to phonon assisted resonant tunneling from one side of the asymmetric double well to the other. The wide variety of local glass configurations is represented by broad distributions of double well asymmetries (energy level splittings) and tunneling parameters (matrix elements coupling the two wells).

In terms of the TLS model, the anomalous capacities of glasses are explained by transitions from the

low energy side of the double well to the high energy side as the temperature is increased [1,2]. For a flat distribution of TLS asymmetries (equal probability of any energy splitting) a contribution to the heat capacity linear in temperature,  $T^1$ , is predicted as an addition to the normal Debye  $T^3$  heat capacity [1,2]. This is close to what is observed experimentally in many glasses. As another example, for chromophores in glasses, exponential photon echo decays with an approximately  $T^1$  temperature dependence can be explained by employing a flat distribution of TLS asymmetries and an approximately flat distribution of tunneling parameters [4,5]. The facts that optical hole widths of chromophores in glasses are wider than the Fourier transform of the corresponding photon echo decays [5] and that the hole widths increase as the time between burning and reading the hole is increased [7] are explained by the broad distribution of fluctuation rates produced by the broad distributions of TLS asymmetries and tunneling parameters [5,8].

The TLS model should be viewed as an approximate way of describing the collection of complex local potential surfaces on which dynamics occur. The essential physical idea is that the local potential surfaces are *fixed*. Dynamics are associated with a very limited number of degrees of freedom. The small structural changes that occur are transitions between

local minima on the fixed potential surface.

A central question in the delineation of the nature of glasses is the validity of the basic concept behind the TLS model, i.e. the fixed potential surface. While the TLS model has had great success in explaining a wide variety of phenomena, other models have also been successful [9,10]. These models involve spatial diffusion of defects or particles or other mechanisms which cause the local potential surfaces to evolve in time. These models are diametrically opposed to the TLS models in that they do not require fixed potential surfaces.

The experiments and associated theory presented below are the first to clearly demonstrate the existence of fixed potential surfaces, and therefore confirm the TLS model. A hole in the spectrum of cresyl violet in ethanol glass is burned and read out at 1.3 K. The temperature is raised to 2.1 K, and the hole is observed to have broadened substantially. At the higher temperature, dynamics which are frozen out at the lower temperature become thermally activated, broadening the hole. When the temperature is returned to 1.3 K, the hole narrows to a value consistent with the temperature and the time between burning and reading. While any of the models of glass dynamics can account for the broadening of the hole when the temperature is raised, only the TLS model, with its fixed potential surfaces, predicts that the hole narrows again when the temperature is lowered. Because the potential surfaces are fixed, changes in structure which occurred at higher temperature are reversed when the sample is returned to the lower temperature. The original low temperature structures are recovered, and the hole is returned to its low temperature width.

## 2. Experiments and results

The experiments are performed in a ethanol glass lightly doped with cresyl violet chromophores. Optical dephasing properties of this system have been studied extensively with photon echoes [11], persistent hole burning [11], and time-dependent hole burning (variation in the waiting,  $T_w$ , time between burning and reading the hole) [7]. Previously, the fluctuation rate distribution at 1.3 K between 0.1 and 5000 s has been mapped out [7].

The sample is prepared by rapid cooling of a solution of  $1.3 \times 10^{-4}$  mol/l cresyl violet 670 perchlorate (Exiton) in anhydrous ethanol in a 1 mm thick spectroscopic cuvette. The cooling rate is sufficiently fast that only the true amorphous glassy state is prepared [5]. During the experiment, the sample is immersed in superfluid  $^4\text{He}$ . The temperature is controlled via the regulation of the  $^4\text{He}$  vapor pressure.

A cw scanning single model dye laser (2 MHz bandwidth) is used to burn and detect (read) spectral holes in the inhomogeneously broadened absorption line. The wavelength of the laser is set at 621 nm, the red edge of the inhomogeneous spectrum. The optical density of the sample is 0.6. The laser beam diameter is 0.4 mm. The burning time and fluence range from 10–30 ms and 20–60  $\mu\text{J}/\text{cm}^2$ , respectively.

At a series of waiting time ( $T_w$ ) after burning, the holes are detected by scanning the dye laser frequency and monitoring the transmission of the laser beam. The reading beam intensity is  $5 \times 10^{-4}$  of the burning. The scan rate is 80 MHz/ms. The detection time is much shorter than the waiting time at all  $T_w$ . The procedure is identical to that of recent time-dependent hole-burning measurements [7].

The time evolutions ( $T_w$  dependence) of hole widths measured at 1.3 K and 2.1 K *without* temperature cycling are shown in fig. 1.  $T_w$  is varied from

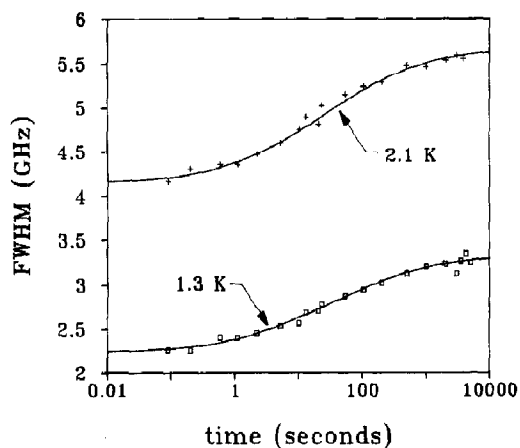


Fig. 1. Time evolutions of the hole widths. Upper trace: burned and detected at 2.1 K. Lower trace: burned and detected at 1.3 K. The solid lines are fit to log-normal fluctuation rate distributions. The fit also provide information about the energy distribution of the TLS.

0.1 to 5000 s. At both temperatures the holes broaden significantly during the observation time interval. As discussed previously for the 1.3 K results [7], the data can be fit (solid lines through the data) to a log-normal fluctuation rate distribution. At the higher temperature, the extent of the fluctuations is greater, yielding broader holes. Details about these measurements will be presented in a subsequent publication. What is relevant to the present paper is that the center rates of the distributions are insensitive to the temperature, and that the short  $T_w$  limit of the hole width follows the same temperature dependence as the photon echo dephasing rate,  $T^{1.2}$  [11].

In the temperature cycling experiment, a hole is burned at 1.3 K. While the spectrum of hole is being measured as a function of  $T_w$ , the temperature is raised to 2.1 K. This temperature is maintained for several minutes, and the hole spectrum is measured. The temperature is then returned to 1.3 K, and hole spectrum measurements are continued. The temperature is changed by varying the vapor pressure of the  $^4\text{He}$  bath. The time intervals for increasing and decreasing the temperature are about 1.5 and 5 min, respectively. Since the superfluid  $^4\text{He}$  has excellent thermal conductivity, the temperature of the sample tracks that of the bath.

The spectral hole is detected *before, during* and *after* the temperature cycling. Spectra of the hole detected during these three time periods are shown in fig. 2. The hole broadens when the temperature is raised, and narrows again when the temperature is decreased. The  $T_w$  dependence during the temperature cycle is plotted in fig. 3. The calculated solid curves from fig. 1 are also plotted as references.

The key feature of the temperature cycling data is that, after returning to the original temperature, the widths of the hole coincide with those observed without going through the temperature cycle. *The line broadening caused by the temperature increase is reversible.*

As will be shown, this behavior indicates that the local fluctuations around a chromophore are about a definite configuration of minimum energy, i.e. there is a global minimum in the glass structure that does not change on the experimental scale. In addition, the structure must be able to relax to its minimum energy configuration within the experimental time scale. This requires the relaxation rates to be either

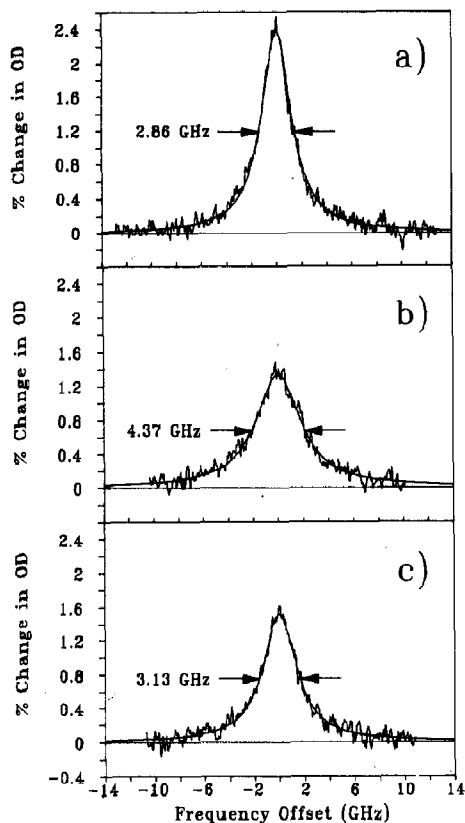


Fig. 2. Effects of temperature cycling on the hole spectra. (a) Hole spectrum at  $T=1.3$  K and  $T_w=20$  s, before temperature increase; (b) at  $T=2.1$  K and  $T_w=160$  s, after temperature increase; and (c)  $T=1.3$  K and  $T_w=2000$  s, after temperature returned to 1.3 K.

much faster than the waiting time or, as is the case here, insensitive to the temperature.

In section 3, the temperature cycling data will be analyzed quantitatively. First, however, the problem will be analyzed qualitatively. The hole is burned at a temperature of  $T_0$ . According to the TLS model, the TLS with energy  $E < kT_0$  are continuously fluctuating between their high and low energy states, while the TLS with  $E > kT_0$  are frozen in their ground states. Therefore, the width of the hole detected shortly after the burning (fig. 3) is induced only by the low energy TLS. When the temperature is raised to  $T_1 > T_0$ , the TLS with  $kT_0 < E < kT_1$  become thermally excited. This causes additional fluctuations that broaden the hole (fig. 3). When the temperature is returned to  $T_0$ , the TLS with  $E > kT_0$  return to their ground states. Thus the component of the config-

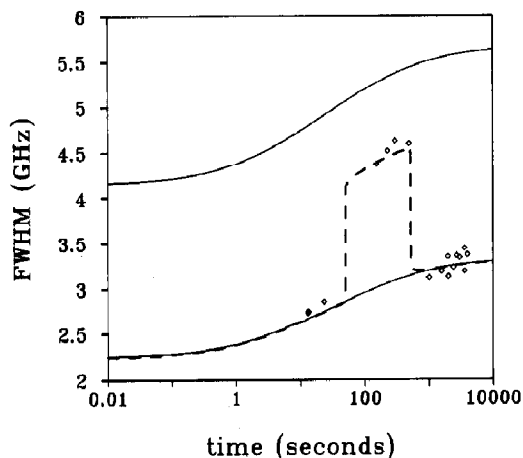


Fig. 3. Time evolution of temperature cycled hole width compared with the theory. ◇: data from three separate experiments. Dashed line: calculation without adjustable parameters using constants obtained from fig. 1 fits. Solid lines: same as those in fig. 1 (shown as reference).

ration which was modified by the dynamics of the high energy TLS at the higher temperature is returned to a state which is identical to that before the temperature cycling. Again, the width of the hole is only induced by the TLS with  $E < kT_0$ . The fixed local potential surface about each chromophore allows the high energy TLS to return to their initial states, and therefore return the chromophore to its initial position in the spectral line. In this manner the hole broadening at the higher temperature can be reversed when the system is returned to the lower temperature.

In contrast, in a particle or defect diffusion model, or in any model in which the local potential surface about each chromophore evolves, there is no specific fixed configuration around each chromophore. After a temperature cycle, for example, diffusing defects do not return to their original positions. The configurations around the chromophores differ from those before the temperature cycling, resulting in permanent shifts of the chromophores' resonance frequencies - *irreversible hole broadening*.

### 3. Theory

In this section, the temperature cycling experiment is analyzed quantitatively as a test of the TLS

model. The TLS model has been successful in describing the results of photon echo and hole-burning measurements in glasses [4-6]. The observed Lorentzian hole shapes and the quasilinear temperature dependence of the hole widths can be derived with the TLS model. However, it is possible to explain previous optical experiments using a defect or particle diffusion model, as has been done for heat capacities [9,10] and other experiments on glasses.

It has been proven [5,8] that the hole spectrum is the Fourier transform of the four point correlation function which describes the stimulated echo [12-14]

$$I(\omega_R - \omega_B; T_w) = F[C(\tau, T_w, \tau)]. \quad (1)$$

For weakly coupled TLS, the four-point correlation function can be rewritten as [8,14]

$$C(\tau, T_w, \tau) = \exp\{-N \langle 1 - \exp[i\varphi(\tau, T_w)] \rangle_{H,r,\lambda}\}, \quad (2)$$

$$\varphi(\tau, T_w) = \Delta\omega \left( \int_0^\tau h(t) dt - \int_{T_w+\tau}^{T_w+2\tau} h(t) dt \right), \quad (2a)$$

where  $N$ , the total number of the TLS in the averaging volume, is assumed to be large. The averages in the exponent are over the random history path,  $H$ , the spatial distribution,  $r$ , and the internal parameters,  $\lambda$  of the TLS.  $\Delta\omega$  is the coupling between the TLS and the chromophore.  $h(t)$  is a random telegram function that only takes on values of  $+1$  and  $-1$ , which accounts for the sign change of the coupling when the TLS changes state.

For hole burning experiments, the waiting time is much longer than the coherence time of the chromophore,  $T_w \gg \tau$ . The history average in this limit becomes [8]

$$\langle 1 - \exp(i\varphi) \rangle_H = p_{+-} [1 - \exp(2i \Delta\omega \tau)] + p_{-+} [1 - \exp(-2i \Delta\omega \tau)], \quad (3)$$

where  $p_{+-}$  ( $p_{-+}$ ) is the joint probability of finding the TLS in the upper (lower) energy state at  $t=0$  and in the lower (upper) energy state at  $t=T_w$ , and can be explicitly written as

$$p_{+-} = \rho_+(0) \rho_- [T_w | \rho_+(0) = 1], \\ p_{-+} = \rho_-(0) \rho_+ [T_w | \rho_-(0) = 1], \quad (4)$$

where  $\rho_+$  ( $\rho_-$ ) is the upper (lower) population of the TLS with respect to its local field. Substituting eq. (4) into eq. (3), we obtain the general result of the history average to be

$$\{\rho_+(0)\rho_-[T_w|\rho_+(0)=1] + \rho_-(0)\rho_+[T_w|\rho_+(0)=1]\}\sin^2(\Delta\omega\tau). \quad (5)$$

Here we have taken into account that the sign of the coupling  $\Delta\omega$  is uncorrelated to the orientation of the local field experienced by the TLS. Therefore, the imaginary parts in eq. (3) cancel.

For dipolar coupling,  $\Delta\omega \approx r^{-3}$ , and a uniform spatial distribution of the TLS, the spatial average can be calculated [5,8]. The four-point correlation function decay is found to be an exponential that results in a Lorentzian hole shape, as is observed. The width of the hole is given by

$$\Delta\omega_H(T_w) \propto \langle \{\rho_+(0)\rho_-[T_w|\rho_+(0)=1] + \rho_-(0)\rho_+[T_w|\rho_+(0)=1]\} \rangle. \quad (6)$$

Thus the entire problem reduces to solving the equation of motion of the TLS.

Since in a hole-burning experiment the line broadening is caused by steady state fluctuations, the regression of the fluctuations, i.e. the motion of a subset of identical TLS, is described by

$$\begin{aligned} \Delta\rho(t) - \Delta\rho(\text{eq}) &= [\Delta\rho(t_0) - \Delta\rho(\text{eq})] \exp[-R(t-t_0)], \\ \Delta\rho &= \rho_+ - \rho_-, \end{aligned} \quad (7)$$

where  $\Delta\rho(\text{eq})$  is the population difference at equilibrium, determined by the Boltzmann distribution, and  $R$  is the relaxation rate towards equilibrium [8].

Take the temperature cycle to be described by a step function,

$$\begin{aligned} T(t) &= T_0, \quad t \leq t_1, \\ &= T_1, \quad t_1 \leq t \leq t_2, \\ &= T_0, \quad t > t_2. \end{aligned} \quad (8)$$

Then the initial probability is  $\rho_+(0) = \rho_+(\text{eq}; T_0)$ . The conditional probability  $\rho_-[T_w|\rho_+(0)=1]$  for the TLS is calculated to be

$$\begin{aligned} \rho_- (\text{eq}; T_0) \{1 - \exp[-R(T_0)T_w]\}, \\ T_w \leq t_1, \end{aligned} \quad (9a)$$

$$\begin{aligned} \rho_- (\text{eq}; T_1) \{1 - \exp[-R(T_1)(T_w - t_1)]\} \\ + \rho_-(t_1) \exp[-R(T_1)(T_w - t_1)], \\ t_1 \leq T_w \leq t_2, \end{aligned} \quad (9b)$$

$$\begin{aligned} \rho_- (\text{eq}; T_0) \{1 - \exp[-R(T_0)(T_w - t_2)]\} \\ + \rho_-(t_2) \exp[-R(T_0)(T_w - t_2)], \\ T_w > t_2. \end{aligned} \quad (9c)$$

One can show that  $\rho_+[T_w|\rho_-(0)=1]$  has the same functional form.

For single phonon assisted resonant tunneling, the relaxation rate is very weakly dependent on the temperature,  $R(T) \sim \coth(E/2kT)$  [1,2]. In the temperature range of interest, it can be taken to be independent of  $T$ ,  $R(T_1) = R(T_0)$ . This is consistent with our experimental observation (see section 2). Thus it is easy to see that eq. (9c) becomes identical to eq. (9a) in the long waiting time limit,  $T_w \gg t_2$ . In practice this condition can always be satisfied in a waiting time-dependent hole-burning measurement because spectral diffusion broadens the hole on a log time scale. Since eq. (9a) describes the situation where no temperature cycling is present, we are led to the conclusion that the temperature cycle does not affect the long time behavior of the hole spectrum.

To calculate the temperature cycling data, it is necessary to average over all of the TLS. Following ref. [8], we reduce the average over the internal parameters of the TLS in eq. (6) to an average over the fluctuation rate distribution. The final expression for the time evolution of the hole width including the temperature cycle is

$$\begin{aligned} \Delta\omega_H(T_w) &= \Delta\omega_0 \langle 1 - \exp(-RT_w) \rangle_R, \\ T_w \leq t_1, \\ &= A \Delta\omega_0 \langle 1 - \exp[-R(T_w - t_1)] \rangle_R \\ &\quad + \Delta\omega_0 \langle \exp[-R(T_w - t_1)] - \exp(-RT_w) \rangle_R, \\ t_1 \leq T_w \leq t_2, \\ &= \Delta\omega_0 \langle 1 - \exp[-R(T_w - t_2)] \\ &\quad + \exp[-R(T_w - t_1)] - \exp(-RT_w) \rangle_R \\ &\quad + A \Delta\omega_0 \langle \exp[-R(T_w - t_2)] \\ &\quad - \exp[-R(T_w - t_1)] \rangle_R, \\ T_w > t_2, \end{aligned} \quad (10)$$

where  $A$  is a scaling constant given by the ratio

$$\frac{\langle \rho_+(eq; T_0) \rho_-(eq; T_1) + \rho_-(eq; T_0) \rho_+(eq; T_1) \rangle_E}{2 \langle \rho_+(eq; T_0) \rho_-(eq; T_0) \rangle_E} \quad (10a)$$

Here we have neglected the temperature dependence of  $R$ .

In fig. 3, eq. (10) is plotted without adjustable parameters (dashed line) using the constants obtained from fitting the standard waiting time-dependent hole-burning measurements (no temperature cycle, fig. 1) at 1.3 and 2.1 K. The temperature cycling times are  $t_1 = 50$  s and  $t_2 = 500$  s. The agreement between experiment and the theory based on the TLS model is quite remarkable.

#### 4. Concluding remarks

The key feature of the experiments and theory presented here is that temperature induced spectral broadening is reversible in a low temperature glass. This implies that the local structures surrounding the chromophores are essentially fixed. The spectral broadening is caused by transitions among local minima on a fixed potential surface. Dynamics on the fixed potential surface can be accurately described using the TLS model. Models in which local structures evolve in time irreversibly will predict irreversible spectral broadening.

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