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Nonlogarithmic spectral diffusion in proteins and glasses

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Abstract

In the first part of the paper, a quantitative theory is developed and new experimental data are presented, which attribute recently observed plateaus in three-pulse photon echoes in glasses to laser heating artifacts. In the second part, the \sqrt{t} -spectral diffusion, recently observed in long time ($t > 3$ h) hole-burning in proteins and glasses, is addressed. Avoiding interacting two-level systems (TLS), we present a model which is supported by MD-simulations and based on the notion of a hierarchical energy landscape. Within it, the algebraic line broadening is connected with the side chain dynamics of the polymer glass and the protein; contrary, the standard logarithmic spectral diffusion (SD) is associated with the collective backbone dynamics. Excellent agreement with experiment is found for both proteins and glasses. The difference between them is attributed to the amount of disorder and organization in their energy landscapes. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Stimulated photon echo time regime

Stimulated photon echo measurements of deuterated ethanol (EtOD) found a slower-than-logarithmic, near constant, increase of the line width with waiting time in the microsecond region, which has been assigned empirically to a gap in the distribution of relaxation rates in the original publication [1]. A recent model by Silbey et al. [2], in contrast, takes a new approach to the problem of nonlogarithmic spectral diffusion. It is based on a numerical simulation of a NiP model glass [3, 4] and uses modified distribution functions for the tunneling matrix element Δ_0 and the energy splittings E of the TLS: $P_{\Delta}(\Delta) = \Delta^{\mu}$ and $P_E(E) = 1/E$.

$\Delta_0^{1-\nu}$. The temperature and time dependence of the line broadening is then given by

$$[1/\pi T_2^*](t) = K_{\nu} T_0^{1+\nu+\mu} (\Theta_{\nu} + (2/\nu) \times [1 - (R_{\text{eff}} t)^{-\nu/2}]) + \Gamma_{\text{PLM}}, \quad (1)$$

where K_{ν} and Θ_{ν} are constants and R_{eff} is an effective relaxation rate (one-phonon rate averaged over E). The last term arises from a pseudo-local phonon mode. Recently, Zilker and Haarer [5] have performed stimulated echo measurements on PMMA below 1 K (see Fig. 1) which showed the existence of sample heating due to the energy of the first two excitation pulses. Since the specific heat c of most glasses is relatively small at low temperatures, typical excitation energies of 20–100 nJ per pulse can already lead to a significant increase of the local temperature T_1 (in EtOD: $T_1 = 2.5$ K for

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an initial temperature of $T_0 = 1.75$ K). After a few hundred microseconds, heat diffusion into the non-illuminated regions of the sample will lead to a return to thermal equilibrium.

In order to incorporate sample heating into Eq. (1), one has to determine the heat flow out of the focal volume of the excitation pulses by solving the heat diffusion equation for the local temperature $T(\mathbf{r}, t)$. Its spatial average is then plugged into the Silbey formalism, implicitly assuming that the phonons are in quasithermal equilibrium with the momentary temperature $T(t)$ in the focal volume. Solving the heat diffusion equation for suitable boundary conditions (heat flow only in radial direction), one finds [6]

$$T(t) = T_0 + (T_1 - T_0) \left\{ \frac{1}{1 + t/\tau_a} - e^{-t/\tau_{fl}} \right\}, \quad (2)$$

where $\tau_{fl} \sim 2 - 10$ ns is the fluorescence lifetime and $\tau_a = a^2 \rho c / \kappa$ is the time constant of heat diffusion out of the focal volume of the laser beam with radius $a \sim 50$ μm (κ is the heat conductivity of the glass). Then, the effective homogeneous line width at the momentary temperature $T(t)$ reads [6]

$$[1/\pi T_2^*(t)] = K_v T_0^{1+v} [\Theta_v + f_v(t, R_{\max}[T(t)]) + \Gamma_{\text{PLM}}, \quad (3)$$

where

$$f_v(t, R_{\max}[T(t)]) = \frac{\int_0^x dx [1 - (t R_{\max}[T(t), x])^{-v/2}] [1 - \tanh(x) \tanh(x T_0/T(t))]}{(v/2) \int_0^x dx x^v \text{sech}^2(x)}. \quad (4)$$

$R_{\max}[T(t), x]$ is the fastest relaxation rate of a TLS with given E .

2. Hole-burning time regime

Recently, Haarer and coworker [7, 8] have performed hole-burning on purified PMMA at 0.5, 1 and 2 K up to extremely long times (from 10 s to 10 days); see Fig. 2. They found a $\log(t)$ -dependence up to about 3 h, but a faster-than-logarithmic

broadening between 3 h and 10 days. The same faster-than-logarithmic broadening has been found in proteins by Friedrich and coworker [9, 10]; see Fig. 3. The protein and the glass data could be fitted with an empirical ad hoc ansatz for the distribution function $P(A, A_0) = P_0 [1/A_0 + A/A_0^2]$ ($A = \text{constant}$), resulting in a growth composed of a superposition of a $\log(t)$ and a \sqrt{t} -term. In both experiments this distribution function has been motivated by the scenario of coherently coupled pairs of TLS's, which was invented by Burin and Kagan [11]. In this formulation the second term stems from pairs of single TLSs which are coupled by a (resonant) up-down transition [11, 12]. An alternative explanation, avoiding the idea of interacting TLS, has been proposed by Heuer and Neu [13]. These authors assumed that due to the long waiting time of the experiment (up to 10 days), the glass explores configurations which are not characterized by the uniform distribution in the tunneling parameter λ of the standard tunneling model (STM). In polymer glasses and proteins a possible origin of these configurations are side chains motions. Based on a numerical analysis of a Lennard-Jones (LJ) model glass, the following extension of the STM has been designed:

$$P(A, V) = \frac{P_0}{E_0} e^{-V^2/2\sigma^2_0} + \sum_{i=1} \frac{P_i}{E_0} e^{-(V-V_i)^2/2\sigma_i^2}. \quad (5)$$

Note that in a simple harmonic oscillator model for each well of the double-well potential (DWP), the tunneling parameter, λ , is related to the barrier height, V , through $\lambda = V/E_0$, where E_0 is the zero-point energy.

3. Results and discussion

Fig. 1 shows the effective homogeneous line width of ZnTPP in PMMA as a function of waiting

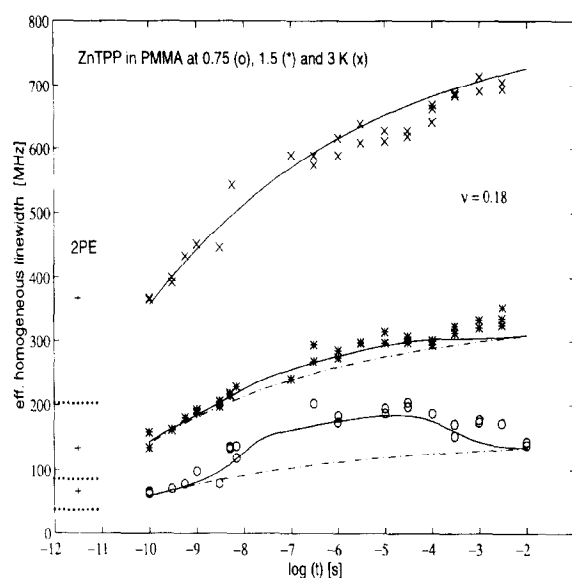


Fig. 1. Line width of the stimulated echo as a function of the waiting time t for ZnTPP in PMMA [5]. For details see text and Ref. [6].

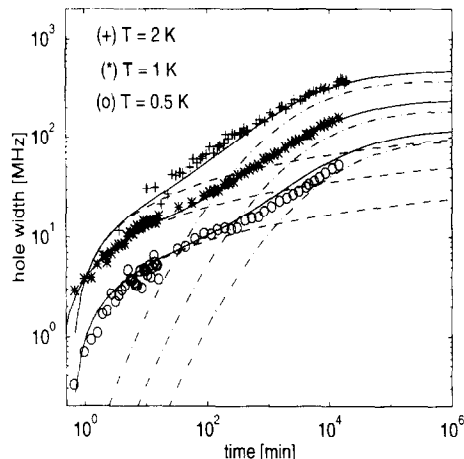


Fig. 2. Hole broadening in the polymer glass PMMA at 2 K (upper curve), 1 K (middle curve), and 0.5 K (lower curve). The experimental data are from Ref. [7,8]. For details see text and Ref. [13].

time t for three different temperatures [5]. The dashed lines are fits with Eq. (1), which neglects sample heating, the straight lines are a fit with Eq. (3), which includes heating. The reason for this

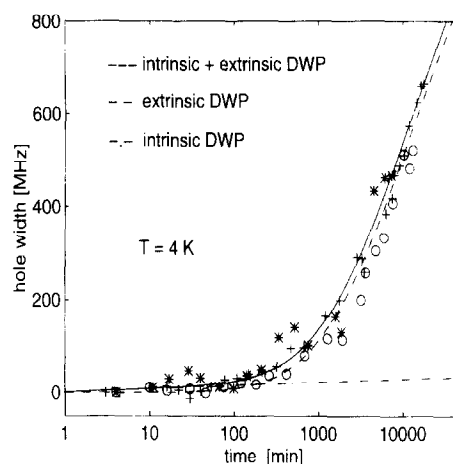


Fig. 3. Hole broadening in the protein cytochrome c. The experimental data are from Ref. [10]: time between cooling and burning: 94 min (+), 4398 min (\circ), and 10093 min (*). For details see text and Ref. [13].

approach becomes immediately evident if one considers the 0.75 K data in more detail. One observes a fast increase of the line width for small waiting times, after about 300 μ s; however, the line width is decreasing with waiting time. This is a clear indication that sample heating has occurred. An estimate from specific heat data yields a maximum temperature $T_1 = 1.3$ K, which is confirmed by our fit, giving $T_1 = 1.5$ K. A fit with Eq. (1) which neglects heating (dashed line) does not adequately describe the data. Since the specific heat of PMMA at 1.5 K is about six times larger than at 0.75 K, heating at the higher temperature is not expected to play such an important role anymore. As can be seen from the data, the differences between both fits are indeed rather small, a specific heat estimate of $T_1 = 1.7$ K is reproduced by our model. At 3 K, finally, there is no sample heating taking place at all.

The three curves can be well described with the same exponent $v = 0.18$; there is no evidence for a gap in the distribution of relaxation rates. The latter may be related to sample heating. Fluency dependent studies on EtOD may provide the final proof for this assumption, whereas today only strong evidence exists.

In Figs. 2 and 3, we compare spectral diffusion broadening derived from Eq. (5) with the

experimental data for PMMA and cytochrome, respectively. In the glasses PMMA logarithmic line broadening occurs below $\sim 10^4$ s, as predicted by the STM. The experimentally detected algebraic \sqrt{t} -time dependence applies approximately between 10^4 and 10^6 s. As is clearly demonstrated in Fig. 2, it arises from a superposition of the two terms in Eq. (5). Hence, the experimentally found exponent 1/2 has no physical significance in this model. The protein data can be fitted without a $\log(t)$ -term (i.e., $P_0 = 0$) as the dashed lines in Fig. 3 illustrate. In any case the contribution of the $\log(t)$ -term is very small as can be inferred from the dash-dotted curve in Fig. 3. This is consistent with the absence of aging observed in Ref. [10] (see data points corresponding to different equilibration times in Fig. 3), which indicates a gap in the distribution of relaxation times between ~ 1 s and 3 h.

4. Concluding remarks

The issue of this contribution was to present new experimental and theoretical results about spectral diffusion in proteins and glasses in the Kelvin regime. Our results reveal that the experiments are sophisticated and not universally describable by the so-called Standard Tunneling Model. The effect of laser heating, interacting TLS, and contamination by defects and side chains have carefully to be taken into account. At present theoretical models are highly speculative; also, experimental evidence of results presented here has to be enhanced: fluency-dependent stimulated photon echoes have to be done to clarify the influence of laser heating; long-

time hole-burning on different polymers and proteins has to be done at different temperatures in order to check out whether TLS–TLS interaction or a hierarchical energy landscape is the physical cause of the observed enhanced spectral diffusion at longer times.

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References

- [1] H.C. Meijers, D.A. Wiersma, *Phys. Rev. Lett.* 68 (1992) 381.
- [2] R.J. Silbey, J.M.A. Koedijk, S. Völker, *J. Chem. Phys.* 105 (1996) 901.
- [3] A. Heuer, R.J. Silbey, *Phys. Rev. Lett.* 70 (1993) 3911.
- [4] A. Heuer, R.J. Silbey, *Phys. Rev. B* 49 (1994) 9411.
- [5] S.J. Zilker, D. Haarer, *Chem. Phys.*, in print, 1997.
- [6] P. Neu, R.J. Silbey, S.J. Zilker, D. Haarer, *Phys. Rev. B* 56 (1997) 11571.
- [7] H. Maier, B.M. Kharlamov, D. Haarer, *Phys. Rev. Lett.* 76 (1996) 2085.
- [8] G. Hannig, H. Maier, D. Haarer, B. Kharlamov, *Mol. Cryst. Liq. Cryst.* 291 (1996) 11.
- [9] J. Gafert, H. Pschierer, J. Friedrich, *Phys. Rev. Lett.* 74 (1995) 3704.
- [10] K. Fritsch, A. Eicker, J. Friedrich, B.M. Kharlamov, J.M. Vanderkooi, *Phys. Rev. Lett.*, submitted.
- [11] A.L. Burin, Yu. Kagan, *JETP* 80 (1995) 761.
- [12] P. Neu, D.R. Reichman, R.J. Silbey, *Phys. Rev. B* 56 (1997) 5250.
- [13] A. Heuer, P. Neu, *J. Chem. Phys.* 107 (1997) 8686.