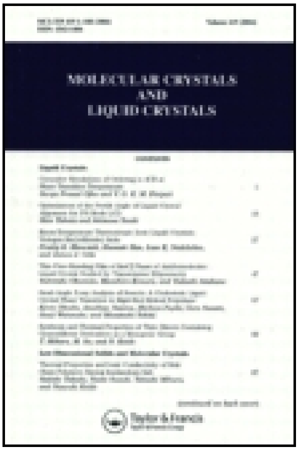

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Stretched Exponential Relaxation and Optical Phenomena in Glasses

D. L. Huber [a]
[a] Department of Physics, University of Wisconsin-Madison, Madison, WI, 53706
Version of record first published: 04 Oct 2006.

To cite this article: D. L. Huber (1996): Stretched Exponential Relaxation and Optical Phenomena in Glasses, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 17-21

To link to this article: http://dx.doi.org/10.1080/10587259608042725

Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 17–21
Reprints available directly from the publisher
Photocopying permitted by license only

STRETCHED EXPONENTIAL RELAXATION AND OPTICAL PHENOMENA IN GLASSES

D. L. HUBER
Department of Physics, University of Wisconsin-Madison, Madison, WI 53706

Abstract A microscopic model for stretched exponential relaxation in glasses and other disordered systems is developed which exploits formal connections with optical phenomena in disordered systems. Two variations of the model are discussed. In the case of static disorder, contact is made with energy transfer in dilute systems; in the dynamic version of the theory, the connection is to the phenomenon of optical dephasing arising from interactions with two-level systems. In both versions, stretched exponential relaxation is related to singular behavior at low frequencies in the density of microscopic relaxation rates. Possible explanations for the singular behavior are assessed.

INTRODUCTION

Stretched exponential, or Kohlrausch [1], relaxation refers to a widely observed phenomenon in disordered materials in which various time-dependent parameters characterizing the macroscopic properties of a system relax to their equilibrium values according to an equation of the form $I(t) \sim \exp[-At^{\alpha}]$, where the non-universal exponent α is positive and less than 1. Microscopic theories describing stretched exponential relaxation fall into two categories depending on whether the relaxation is hierarchical [2] or parallel. In this note, we review recent developments in a theory based on the concept of parallel relaxation [3]. Particular emphasis is placed on those aspects of the theory that display a formal similarity to theories of the dynamics of optical excitation in disordered systems.

In the case of parallel relaxation, a further subdivision can be made into models where the disorder is static and those where dynamical effects are important. The analysis in Ref. 3 was based on a static model in which the total relaxation rate was written as a sum of microscopic 'channel' relaxation rates, i.e. $W = \Sigma_j w_j$, where the symbol w_j refers to the relaxation rate of the jth channel. It was assumed that the relaxation takes place locally and that the number of locally active channels varied throughout the system. Using a theoretical approach analogous to that employed in the theory of unidirectional energy transfer in dilute systems, where the fluorescence varies as $\exp[-At^{1/2}]$ (in the case of dipole-dipole coupling), an expression for the decay was derived of the form

$$I(t) = \exp[-\int_0^\infty dw \rho_w(w)(1-\exp[-wt])], \tag{1}$$

where $\rho_w(w)$ is the density of active channels, and $I(t)$ is normalized to its value at $t = 0$. It was pointed out that asymptotic stretched exponential relaxation reflected singular behavior in $\rho_w(w)$ as $w \to 0$, i.e. $\rho_w(w) \sim w^{-(\alpha+1)}$. Recently, alternative derivations of Eq. (1) have been given based on the theory of random point processes [4] and Poissonian statistics. [5]

A dynamical extension of the static model of parallel relaxation has been developed which treats the relaxation rates as time-dependent random variables fluctuating between the values 0 and 1. [6] It was assumed that the fluctuations arise from thermally activated gates that open and close at random with transition rates that satisfy detailed balancing conditions. It was further assumed that the probability of any individual channel being open was vanishingly small, although the spectral density of open channels was finite. Using a formalism analogous to that developed to treat optical dephasing in glasses coming from interactions of the chromophores with two-level systems (where transitions of the two-level systems induce discrete fluctuations in the optical frequency of the chromphore), [7] it was shown that $I(t)$ varied as

$$I(t) = \exp[-\int_0^\infty dw \int_0^\infty dR \rho_{wR}(w,R)(\frac{w^2}{(w+R)^2})(1-\exp[-(w+R)t])], \tag{2}$$

where R is the gate transition rate associated with switching from 'open' to 'closed' and ρ_{wR} is the channel density. With the aid of a Tauberian theorem [8], it was established that stretched exponential behavior in $I(t)$ corresponded to the function $f(x)$, which is defined by the equation

$$f(x) = x^{-1}\int_0^x w^2 \rho_{wR}(w, x-w)dw\,, \tag{3}$$

varying as $x^{-\alpha}$ as $x \to 0$.

MICROSCOPIC MECHANISMS

The results presented in the preceding section establish a connection between stretched exponential relaxation and anomalies in the distribution of low frequency relaxation modes. To make this connection more precise in the case of static disorder, we take the time derivative of the logarithm of Eq. (1). Assuming asymptotic stretched exponential relaxation, we obtain the equation

$$\alpha A t^{\alpha-1} = \int_0^\infty dw w \rho_w(w)\exp[-wt]\,. \tag{4}$$

for $t \to \infty$. Again employing a Tauberian theorem [8], one obtains the result

$$\rho_w(w) \to A\alpha w^{-(\alpha+1)}\Gamma(1-\alpha)^{-1},\ w \to +0, \tag{5}$$

which makes explicit the connection between the asymptotic behavior of $I(t)$ and $\rho_w(w)$ (here $\Gamma(x)$ denotes the gamma function).

Assuming the parallel relaxation model is appropriate, the question naturally arises as to the microscopic relaxation mechanism that gives rise to singular behavior in $\rho_w(w)$. A common relaxation mechanism encountered in solids involves thermal activation and/or tunneling. The corresponding microscopic rate is of the form $\Omega\exp[-U(T)]$, where Ω is an attempt frequency and the parameter U is temperature-dependent, varying as E_{act}/kT at high temperatures, where E_{act} is an activation energy, and approaching a constant value in the zero-temperature, tunneling limit. Assuming the density of relaxation rates is dominated by the exponential dependence of w on U, one obtains a corresponding distribution for U [9]:

$$\rho_U(U) = A\alpha\Omega^{-\alpha}\exp[\alpha U]\Gamma(1-\alpha)^{-1},\ U \to \infty. \quad (6)$$

A second mechanism, which is suggested by the energy transfer model mentioned in the Introduction, may be appropriate when the macroscopic quantity whose decay is described by $I(t)$ is a sum of local quantities, e.g. local polarizations, local distortions, etc.. If the local quantities relax by the transfer of excitation to localized, randomly distributed fast relaxing centers at a rate which varies as $\lambda r^{-\sigma}$, where r is the separation, then a calculation analogous to that in Ref. 3 leads to the result

$$\rho_w(w) = 4\pi N\sigma^{-1}\lambda^{3/\sigma}w^{-(1+3/\sigma)}, \quad (7)$$

where N is the spatial density of fast relaxing centers. Comparing Eq. (7) with Eq. (5), we infer that $\alpha = 3/\sigma$. Two comments are relevant here: first, in order for the average relaxation rate, $N\int d\mathbf{r}(\lambda/r^{\sigma})$, to be finite in a macroscopic system, one must have $\sigma > 3$. If this is the case, one has $0 < \alpha < 1$; second, if the distribution of fast relaxing centers is characterized by an effective (fractal) dimension, d_f ($d_f < 3$), one has $\alpha = d_f/\sigma$ [4,10].

DISCUSSION

Of the two microscopic mechanisms for asymptotic stretched exponential that are mentioned above, the one based on thermal activation/tunneling seems less probable since it requires a distribution of activation energies/tunneling parameters that increases exponentially with U. The mechanism based on cross relaxation to randomly distributed, rapidly relaxing centers appears more plausible. However, since the transfer to distant centers probably involves dipole-dipole or shorter range interactions, the minimum value of σ is likely to be 6 in most situations (as it usually is for optical energy transfer in dilute systems). As a consequence, α is predicted to be less than or equal to 0.5 for the static cross relaxation model. Whether a dynamical model based on the cross transfer picture can give rise to α greater than 0.5 remains to be established.

ACKNOWLEDGMENTS

The author would like to thank Dr. M. O. Vlad for rekindling his interest in stretched exponential relaxation. Research supported in part by the National Science Foundation.

REFERENCES

1. R. Kohlrausch, Ann. Phys. (Leipzig), 12, 393 (1847).
2. R. G. Palmer, D. Stein, E. S. Abrahams and P. W. Anderson, Phys. Rev. Lett., 53, 958 (1984).
3. D. L. Huber, Phys. Rev. B, 31,6070 (1985).
4. M. O. Vlad and M. C. Mackey, J. Math. Phys., 36, 1834 (1995).
5. D. L. Huber and M. O. Vlad (unpublished).
6. D. L. Huber, Phys. Rev. E, 53, 6544 (1996). See also M. O. Vlad, R. Metzler, T. Nonnenmacher and M. C. Mackey, J. Math. Phys., 37, 2279 (1996).
7. D. L. Huber, J. Lumin., 36, 307 (1987).
8. L. Frennemo, Math. Scand., 20, 225 (1967) and references therein.
9. M. O. Vlad, D. L. Huber and J. Ross (unpublished).
10. J. Klafter and M. F. Shlesinger, Proc. Nat'l. Acad. Sci. USA, 83, 848 (1986).