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## Relaxation in disordered systems†

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Non-exponential relaxation in disordered systems may be interpreted in terms of a distribution of exponential rate constants that arises naturally from a narrow, random distribution in the value of a structural parameter (distance or angle) which characterizes the inequivalent sites within the system. This analysis is applied to the decay of methyl radicals in glassy methanol and to other systems. In the former case, the underlying assumptions have been tested experimentally. Such an approach indicates in general terms which kind of disorder is responsible for the observed decay. It also offers the prospect of obtaining a detailed description of the microscopic structure of a reactive site.

### 1. Order in disorder

All ordered systems resemble each other, but each disordered system seems to be disordered in its own way; that is, the pattern of organization in structurally ordered systems is easily appreciated, but the notion that a pattern can be discerned in the manner in which disordered systems deviate from perfect order remains largely hypothetical. To find some order in disorder is a formidable challenge to theorists and experimentalists alike, and one that will require a good deal of interaction between them. In this article, we look at disorder by following relaxation processes. Theoretically, this may not seem to be a promising approach because relaxation is a complicated, dynamic process that often is not easy to fathom in an ordered system. Experiments tell us, however, that many relaxation processes in disordered systems follow a common pattern; they proceed non-exponentially in such a way that the effective rate constant seems to decrease in time, the so-called 'stretched exponential' decay. In ordered systems, such as crystals, the 'sites' (atoms, molecules, etc.) relax in random order, leading to an exponentially decaying signal. Paradoxically, in a disordered system, the sites relax in a hierarchical order because disorder makes the sites different. Thus non-exponential relaxation measures these differences and, since relaxation rates are often extremely sensitive to structural differences, it measures them very accurately.

### 2. Connection between structure and relaxation rate

It is not difficult to put these ideas into a mathematical form. We start from the assumption that, in a perfectly ordered system, the relaxation is exponential with a rate constant  $k_0$ . We then introduce structural disorder such that a structural parameter, which has the value  $R_0$  in the crystal, assumes a distribution of  $R$ -values. We shall assume that the rate constant  $k$  varies exponentially with  $R$ :

$$k = k_0 \exp[-\lambda(R - R_0)] \quad (1)$$

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Such a dependence is very common for rate processes and can be derived, at least for  $|R - R_0| \ll R_0$ , for a variety of models (Siebrand *et al.* 1983, 1984, Doba *et al.* 1984 a, b).

To complete the picture, we need to assume a distribution of  $R$  values,  $\Phi(R)$ . If the distribution is narrow, i.e., if  $|R - R_0| \ll R_0$ , and if the deviations  $R - R_0$  are random and independent of each other,  $\Phi(R)$  will be a Gaussian

$$\Phi(R) = \pi^{-1/2} \Gamma^{-1} \exp[-(R - R_0)^2 / \Gamma^2] \quad (2)$$

where  $\Gamma$  is the halfwidth of the distribution. By substituting (1) into (2) subject to  $|\Phi(R)dR| = |F(k)dk|$ , we get the distribution of rate constants

$$F(k) = \pi^{-1/2} (k\lambda\Gamma)^{-1} \exp\{-[\ln(k/k_0)]^2 / \lambda^2 \Gamma^2\} \quad (3)$$

The time dependence of the relaxation process will then be given by the Laplace transform of  $F(k)$ :

$$f(t) = \int_0^\infty F(k) \exp(-kt) dk \quad (4)$$

so that

$$f(t) = \pi^{-1/2} \gamma^{-1} \int_{-\infty}^\infty \exp(-x^2/\gamma^2 - k_0 t \exp x) dx \quad (5)$$

where  $x = \ln(k/k_0) = -\lambda(R - R_0)$  and  $\gamma = \lambda\Gamma$ .

Although this integral must be evaluated numerically, which is clearly a disadvantage, the result is simple enough to allow direct comparison with experiment. It involves two unknown parameters:  $k_0$ , the rate constant corresponding to the 'average' structure  $R_0$ , and  $\gamma$ , the halfwidth of the gaussian distribution of  $\ln k$  values. These parameters are usually not known *a priori*, but must be derived from the data. Hence an extensive data set is generally required to obtain meaningful results.

### 3. Some examples

As a first application, we consider methyl radicals in a methanol glass. A radical abstracts a hydrogen atom from the methyl group of methanol, thereby turning into a methane molecule. The glass is, of course, a disordered system and the methyl radical signal decays non-exponentially (Bol'shakov and Tolkatchev 1976, Stepanov *et al.* 1978, Bol'shakov *et al.* 1980, Vyazkovkin *et al.* 1983, Doba *et al.* 1983, 1984 a, b, 1985). The hydrogen transfer proceeds by tunnelling. The application of equation (1), which states that the tunnelling rate constant varies exponentially with the tunnelling distance, is supported by explicit model calculations for this system; these calculations account satisfactorily for the observed temperature and isotope dependence of the tunnelling rate constant (Doba *et al.* 1984 a, b). The assumption that we are dealing with a distribution of exponential rate constants can also be tested for this system, since the distribution can be altered by the way we prepare the radicals. Normally, they are prepared photochemically by illumination for a period short compared to the relaxation time. We can change the distribution in a controlled way by longer illumination with reduced intensities. The predicted change in the relaxation is confirmed by actual observations, as expected for a distribution of exponential rate constants (Doba *et al.* 1983, 1984 b). Hence, we have independent evidence that equations (1) and (4) apply, so that comparison with (5) should amount to a test of equation (3). Such a comparison is shown in figure 1. Clearly, equation (5) can provide a

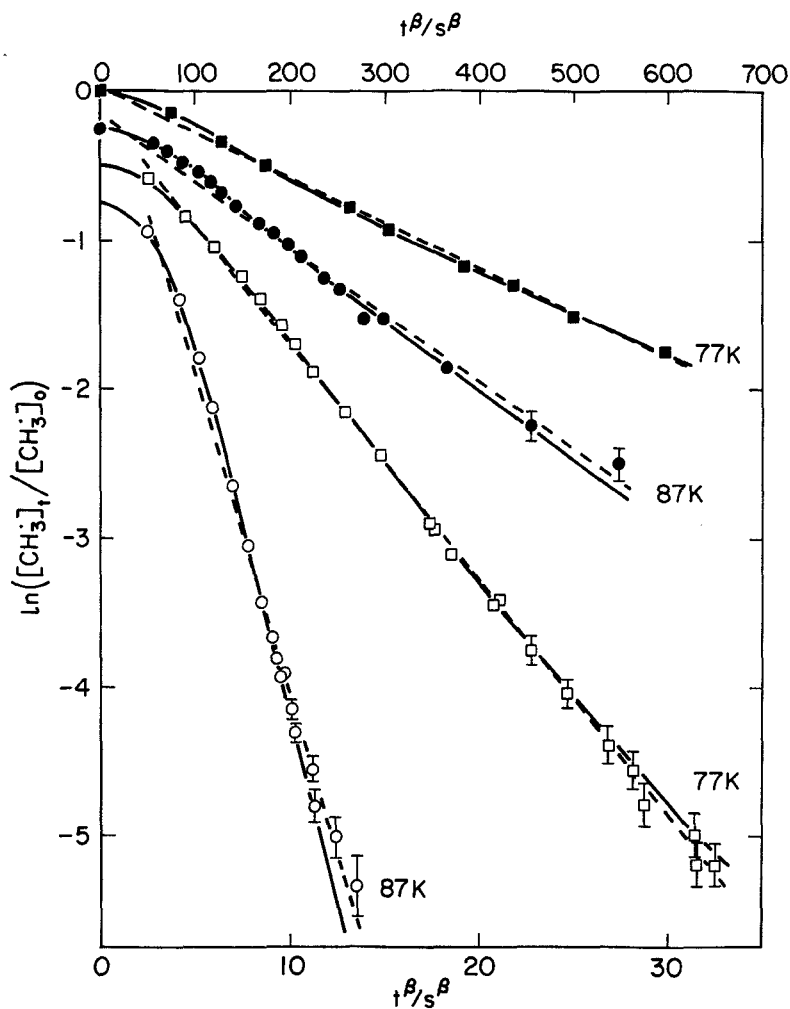


Figure 1. Decay of methyl radicals in methanol glass plotted semilogarithmically against  $t^\beta$ , where  $\beta = \sigma/(1 + \sigma)$  is chosen to give the best fit to equation (6). Open (solid) symbols and the lower (upper) abscissa correspond to hydrogen (deuterium) transfer. Solid curves and broken lines represent the best least-squares fits obtained with equations (5) and (6), respectively.

good fit to the experimental data, confirming the assumed gaussian distribution of hydrogen tunnelling distances in the glass. A similar analysis of the decay of trifluoromethyl radicals yields comparable fits (Doba and Wildman, unpublished).

Is it possible to extract more detailed information from the decay curves? For methyl radicals trapped in glassy methanol, this is indeed the case. Analysis of the temperature and isotope dependences of  $k_0$ , with the aid of a suitable model for the reaction, indicates a value for  $R_0$  which allows us to evaluate  $\lambda$  theoretically. Thus, we can obtain a value for the halfwidth,  $\Gamma$ , of the distribution of tunnelling distances. This result can be tested theoretically by computer simulation of the glassy solution. We can go further by studying mixtures of  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$ , for which the distribution

$\Phi(R)$  is isotope-independent. A detailed treatment of such systems is beyond the scope of this article; however, these simple arguments show the power of the analysis based on equations (1), (2) and (4).

We now consider three additional applications: decay of a photochemical hole, dielectric relaxation in an orientationally disordered solid, and haeme-ligand rebinding at low temperatures.

The plot in figure 2 refers to photochemical hole burning. Site-selective excitation of dye molecules in a matrix leads to shifts of the absorption band of the excited molecule due to local photochemistry (Breinl *et al.* 1984). As a result, a hole is burned in the inhomogeneously broadened absorption band. Relaxation of the dye leads to disappearance of the hole: this process is non-exponential and is reasonably well described by equation (5). However, the range of signal strengths is not large.

The plot in figure 3 refers to dielectric relaxation of orientationally disordered, hexagonal ice Ih, which involves rotation of polar molecules (Gough and Davidson 1970). The process is again non-exponential in time, but the plot is different from those in figures 1 and 2 because the relaxation is measured as a function of frequency: figure 3 shows the absorptive component of the complex dielectric constant. Again, the solid curve obtained from equation (5) appears to give a reasonable fit.

The plot in figure 4 refers to recombination of carbon monoxide with the haeme prosthetic group in myoglobin at low temperatures (Siebrand *et al.* 1985). The system is prepared by photodissociation of the haeme-ligand complex under conditions such

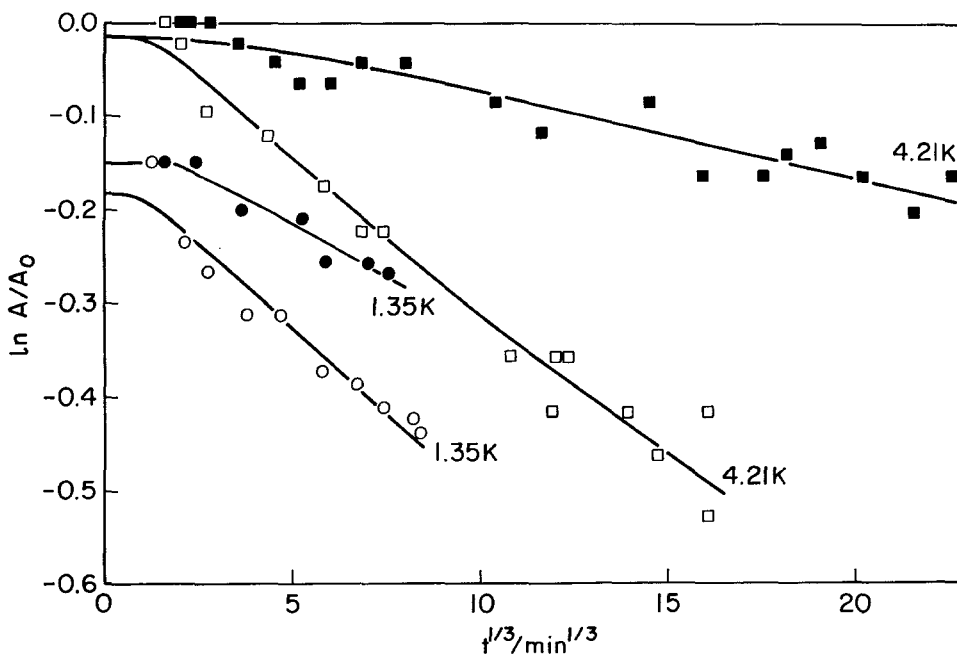


Figure 2. Decay of the area of a photochemical hole in the absorption spectrum of 1,4-dihydroxyanthraquinone in 3:1 ethanol-methanol glass. Open (solid) symbols correspond to hydrogen (deuterium) transfer. Solid curves represent the best least-squares fits obtained with equation (5).

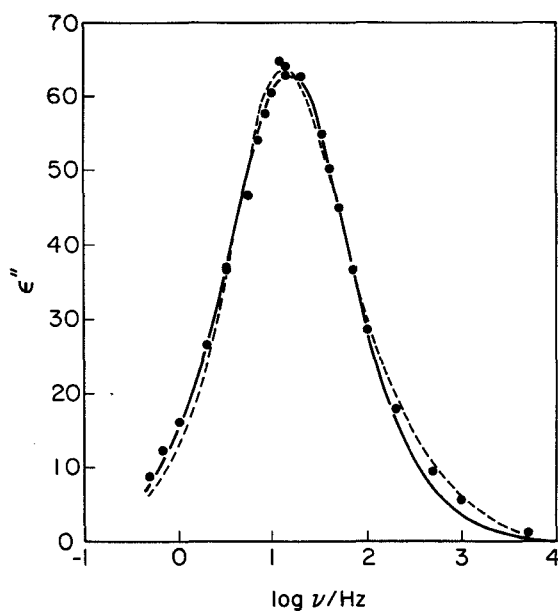


Figure 3. Dielectric loss curve for ice Ih at 181 K and 110 bar pressure. Solid and broken curves represent the best least-squares fits obtained with equations (5) and (6), respectively.

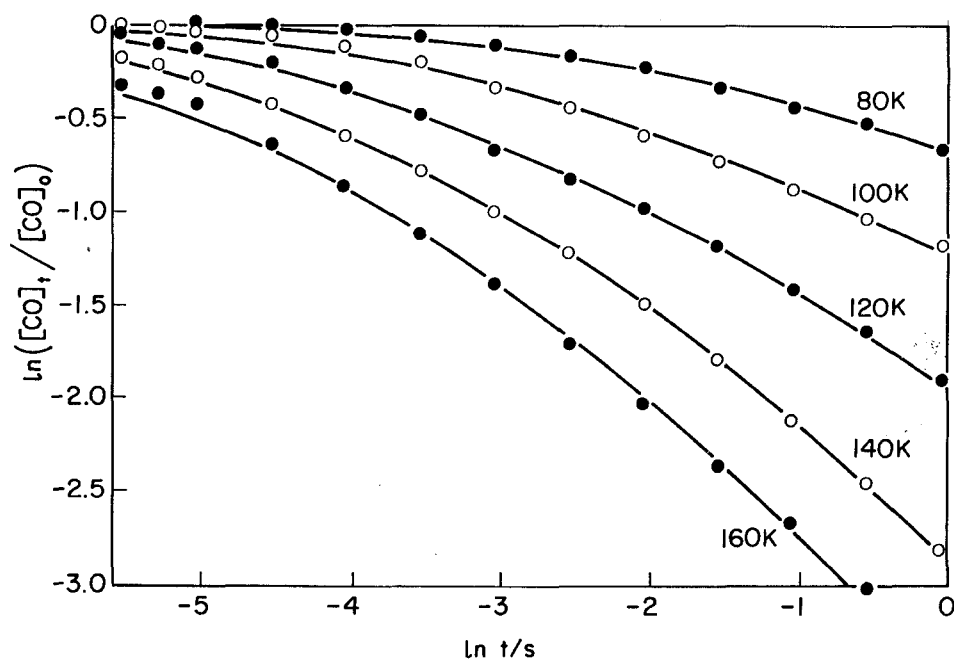


Figure 4. Decay of carbon monoxide concentration through geminate recombination with the haeme in myoglobin. Solid curves represent the best least-squares fits obtained with equation (5).

that the CO molecule remains trapped inside the haeme pocket (Austin *et al.* 1975, Alberding *et al.* 1976, Beece *et al.* 1980, Dlott *et al.* 1983). This reaction resembles that leading to photochemical hole burning. A good, if imperfect, fit is obtained.

#### 4. The rate constant distribution

Although this group of examples can easily be extended, it is large enough to indicate that the present analysis is meaningful. It would be premature to claim that a universal equation has been found to account for all relaxation processes in disordered systems. We therefore limit ourselves to the claim that the present approach opens the way to relate non-exponential relaxation to structural disorder. It has been common practice to describe disorder in dynamic terms, such as a distribution of potential energy barriers. These, however, are derived quantities that cannot be directly observed. Clearly an interpretation in structural terms brings us much closer to the basis of disorder.

An empirical relation that has frequently been used to describe non-exponential relaxation is the 'stretched exponential' function

$$f(t) = \exp[-(t/\tau_{\text{eff}})^{\sigma/(1+\sigma)}] \quad (6)$$

where  $\sigma > 0$  and  $\tau_{\text{eff}}$  is an effective relaxation time (Kohlrausch 1847, Williams and Watts 1970, Williams *et al.* 1971). The corresponding distribution  $F(1/\tau)$  can be obtained by an inverse Laplace transformation, which yields, to a good approximation,

$$F(1/\tau) = F(1/\tau_0) \left(\frac{\tau}{\tau_0}\right)^{1+1/2\sigma} \exp\left\{\left(\frac{1}{2} + \frac{1}{\sigma}\right)\left[1 - \left(\frac{\tau}{\tau_0}\right)^\sigma\right]\right\} \quad (7)$$

where  $\tau_0$  corresponds to the peak in  $F(1/\tau)$  (Helfand 1983). This result is exact for  $\sigma = 1$  and satisfactory for other values of  $\sigma$ , except in the physically insignificant regions near  $F(1/\tau) = 0$  and  $\sigma = 0$ . There have been a number of efforts to 'derive' equation (6) from physical models, none of them very convincing (Ngai 1979, 1980, Cohen and Grest 1981, Shlesinger and Montroll 1984, Palmer *et al.* 1984, Rajagopal *et al.* 1984). Furthermore, this equation goes to the wrong limit ( $df(t)/dt \rightarrow \infty$  as  $t \rightarrow 0$ ) and the distribution (7) does not yield a finite average value of  $k$ . If we ignore these difficulties and interpret (7) by means of (1), we get

$$F(1/\tau) = F(1/\tau_0) \exp\left[\left(\frac{1}{2} + \frac{1}{\sigma}\right)\{1 - \sigma x - \exp(-\sigma x)\}\right] \quad (8)$$

For small  $|x|$ , equation (8) reduces to

$$F(1/\tau) \simeq F(1/\tau_0) \exp\left[-\frac{1}{4}\sigma(2+\sigma)x^2\right] \quad (9)$$

i.e., a gaussian with a halfwidth  $2/[\sigma(2+\sigma)]^{1/2}$ . For large  $x$ , i.e., small  $R$ , we obtain instead

$$F(1/\tau) \simeq F(1/\tau_0) \exp\left(\frac{1}{2} + 1/\sigma\right) \exp\left[-(1 + \frac{1}{2}\sigma)x\right] \quad (10)$$

i.e., an exponential distribution. Hence, the main difference between equations (5) and (6) lies in their behaviour for small  $R$ , i.e., at short times. Since short-time results may be uncertain because of slow instrument response and long-time results suffer from low signal-to-noise ratios, the success of the empirical equation (6) can be qualitatively understood on the basis of its similarity to equation (5). This is confirmed by numerical comparisons.

## 5. Conclusion

In this article, we have interpreted non-exponential relaxation behaviour in various systems in terms of structural disorder. The main result is not only a new equation, but especially a new viewpoint. We assume that the observed, non-exponential decay is a linear superposition of the fundamental, exponential decays and that each of these in turn corresponds to a particular structural arrangement. This feature unifies the various examples presented above. Potentially, an approach of this kind allows a detailed description of the microscopic structure of the disordered system in the neighbourhood of a reactive site. The examples quoted indicate that, in many cases, the structural disorder can be described, to a first approximation, as due to small, random and independent deviations from local order.

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