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Statistical model for stretched exponential relaxation in macroscopic systems

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We develop a statistical model for the stretched exponential relaxation, $\exp[-(t/\tau)^{\alpha}]$, observed in many macroscopic systems. The model, which is suggested by theories for the decay of luminescence in the presence of a random distribution of traps, is applicable in two cases. The macroscopic system is composed of a number of similar, weakly interacting subsystems all of which are characterized by the same set of relaxation channels and rates, with the subsystems differing from one another in the channels which are blocked. Alternatively, the model is appropriate to a situation where the relaxation channels open and close randomly in time with the correlation times for the fluctuations being long in comparison with the reciprocals of the corresponding rates. The parameter α characterizing the relaxation is related to the limiting behavior of a weighted density of relaxation rates. As a special case, the model reproduces results obtained previously for luminescence decay at low trap concentration.

In recent years attention has been drawn to the nonexponential relaxation of various nonequilibrium parameters of macroscopic systems. Ngai[1] has emphasized the widespread appearance of the so-called Kohlrausch[2] or stretched-exponential relaxation where the asymptotic time dependence takes the form

$$I(t)=I_0\exp[-(t/\tau)^{\alpha}],\quad 0<\alpha<1. \tag{1}$$

A variety of theories have been proposed to account for this time dependence.[1,3–6] Some of these are statistical in character.[3,4] The theory outlined in Ref. 6 is fundamentally different from the others, however, in that it involves hierarchically constrained dynamics. It is fair to say that no one of these theories is truly universal in the sense that it is appropriate for all situations where stretched-exponential decay is observed.

The purpose of this paper is to present a new theory for the stretched-exponential decay. While statistical in nature, it is distinct from the other statistical theories which have been proposed. Although theory is suggested by a model for the decay of optical fluorescence in the presence of a random distribution of trapping centers,[7–10] it is applicable in other situations as well.

The theory is appropriate for two distinct cases. The first of these is when the macroscopic body can be divided into a number of similar, weakly interacting subsystems. All of these subsystems are characterized by the same set of potential relaxation channels and rates, which we label by $\nu=1,2,\ldots$. The subsystems differ from one another in the various channels which are blocked due to varying microscopic environments. Writing the relaxation rate associated with channel ν as W_ν, we have the time dependence

$$I(t)=I_0\left\langle \exp\left[-\sum_\nu W_\nu t\right]\right\rangle , \tag{2}$$

where the brackets indicate an average over the ensemble of subsystems. Denoting by P_ν the fraction of subsystems which have channel ν open, we can write the configurational average in the form[9,10]

$$I(t)=I_0\prod_\nu (1-P_\nu+P_\nu e^{-W_\nu t}) . \tag{3}$$

The result, Eq. (3), is also obtained when the various relaxation channels of a single system open and close randomly in time due to fluctuations in the interaction with its environment. When there is no correlation between different channels the decay is associated with the product of the average of factors of the form

$$\exp\left[-\int_0^t w_\nu(t')\,dt'\right] ,$$

where w_ν fluctuates between the values W_ν and 0. A standard Markovian analysis[11] shows that Eq. (13) is obtained when the correlation time for fluctuations in the opening and closing of the νth channel is long in comparison with W_ν^{-1}. In this case P_ν is the fraction of time the νth channel is open.

In our model stretched-exponential behavior requires that there be a continuum of channels with a small probability of any one of them being open. In this case we have

$$\begin{aligned}\prod_\nu (1-P_\nu+P_\nu e^{-W_\nu t}) &= \exp\left[\sum_\nu \ln(1-P_\nu+P_\nu e^{-W_\nu t})\right] ,\\ &\simeq \exp\left[-\sum_\nu P_\nu(1-e^{-W_\nu t})\right] ,\\ &\simeq \exp\left[-\int_0^\infty \bar{\rho}(W)(1-e^{-Wt})\,dW\right] ,\end{aligned} \tag{4}$$

where $\bar{\rho}(W)$, a weighted density of relaxation rates, is given by

$$\bar{\rho}(W)=\sum_\nu P_\nu \delta(W-W_\nu) . \tag{5}$$

In the model under discussion asymptotic stretched-exponential decay is associated with singular behavior in $\bar{\rho}(W)$ as $W\to 0$. With $\bar{\rho}(W)\sim CW^{-\alpha-1}$ we have

$$\int_0^\infty \bar{\rho}(W)(1-e^{-Wt})\,dW \sim C\alpha^{-1}t^{\alpha}\Gamma(1-\alpha)+\cdots . \tag{6}$$

In Eq. (6) Γ denotes the gamma function, and the terms omitted vary less rapidly than t^α. The requirement that the initial slope of $I(t)/I(0)$

$$\frac{d}{dt}I(t)/I(0)|_{t=0} = -\sum_{\nu} P_\nu W_\nu = -\int_0^\infty W\bar{p}(W)dW \ , \tag{7}$$

be finite leads to the condition that $\alpha < 1$.

The other limit on α follows from the fact that

$$\prod_{\nu}(1-P_\nu+P_\nu e^{-W_\nu}) \approx \exp\left[-\sum_{\nu} P_\nu\right] \ , \tag{8}$$

as $t \rightarrow \infty$. Thus $I(t)$ will relax to zero only if the integral

$$\int_0^\infty \bar{p}(W)dW \ ,$$

is infinite. Such will be the case when $\alpha > 0$. Shifting the nonintegrable singularity in $\bar{p}(W)$ to a point other than the origin is ruled out since it gives rise to an infinite initial slope [cf. Eq. (7)]. Similar arguments also rule out an infinity associated with the upper limit to the integral of $\bar{p}(W)$; i.e., it would also give rise to an infinity in the integral of $W\bar{p}(W)$.

As noted earlier, the theory outlined above is suggested by a model for the decay of luminescence in the presence of a random distribution of trapping centers. We make contact with the approach of Refs. 7–10 by pointing out that in this case the relaxation channels are associated with traps on the lattice sites in the neighborhood of the fluorescing ion. Relaxation via the νth channel involves the nonradiative transfer of excitation to a trap on lattice site ν, while P_ν is identified with c, the probability that site ν is occupied by a trap. Assuming the transfer takes via the dipole-dipole mechanism, then $W_\nu = \beta r_{0\nu}^{-6}$, where β is a material-dependent parameter and $r_{0\nu}$ is the separation between the excited ion and the trap. In this case Eq. (4) takes the form ($c << 1$)

$$\prod_{\nu}(1-c+ce^{-\beta t/r_{0\nu}^6}) \simeq \exp\left[-c\sum_{\nu}(1-e^{-\beta t/r_{0\nu}^6})\right] \ . \tag{9}$$

Converting the sum over lattice sites ν to an integral over r we have

$$c\sum_{\nu}(1-e^{-\beta t/r_{0\nu}^6}) \rightarrow 4\pi n_T \int_{r_{\min}}^\infty r^2 dr(1-e^{-\beta t/r^6}) \ , \tag{10}$$

where n_T is the trap density and $r_{\min}$ is a cutoff associated with the maximum transfer rate. Taking the variable of integration to be β/r^6 we can write the right-hand side of Eq. (7) in the form

$$(2\pi n_T/3)\beta^{1/2}\int_0^{W_{\max}} W^{-3/2}(1-e^{-Wt})dW \ ,$$

where $W_{\max} = \beta/r_{\min}^6$. From this expression we identify the weighted density of relaxation rates

$$\bar{p}(W) = (2\pi n_T/3)\beta^{1/2}W^{-3/2}, \ \ 0 < W < W_{\max} \ , \tag{11}$$

corresponding to $\alpha = \frac{1}{2}$ and thus $I(t)$ varying asymptotically as $\exp[-(t/\tau)^{1/2}]$.[7]

In summary, we have outlined a model for stretched-exponential relaxation. Although the assumptions of the model are quite restrictive, it may be appropriate for phenomena other than the decay of luminescence.

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