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Dynamical model for stretched exponential relaxation in solids

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A dynamical model for stretched exponential relaxation in solids is developed. The essential assumption is that the relaxation of a macroscopic parameter can take place simultaneously via a large number of channels, each of which is controlled by a thermally activated ''gate'' that opens and closes at random with transition rates that satisfy detailed balancing conditions. It is further assumed that the probability of any individual channel being open is vanishingly small, although the spectral density of open channels is finite. It is shown that in the model, stretched exponential relaxation reflects scaling behavior in the joint distribution of relaxation rates and transition rates for the open channels. The behavior is similar to an analogous static model treated previously and reduces to that of the static model when the transition rates for the gates approach zero. [S1063-651X(96)05106-9]

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I. INTRODUCTION

Although the existence of Kohlrausch [1] or ''stretched exponential'' ($\exp[-(t/\tau)^\alpha]$, $0<\alpha<1$) decay of various nonequilibrium parameters characterizing macroscopic systems is well established, an understanding of the origin of this behavior is still not complete. This is largely a consequence of the fact that a variety of microscopic mechanisms can give rise to stretched exponential relaxation. In a previous paper [2], we proposed a static model for the decay that was based on an analogy with the decay of the fluorescence in a system with a random distribution of trapping centers. In the approach followed in Ref. [2], the relaxation could take place simultaneously via a number of channels that were labeled by the symbol ν. It was assumed to take place locally on a microscopic scale; however, the probability of a channel being open, P_ν, varied randomly throughout the system. Thus the time dependence of the relaxation was assumed to be governed by an equation of the form

$$l(t)=l_0\left\langle \exp\left[-\sum_\nu W_\nu t\right]\right\rangle, \tag{1}$$

where W_ν is the relaxation rate associated with the νth channel, and the angular brackets denote a configurational average. This average can be written

$$l(t)=l_0\prod_\nu (1-P_\nu+P_\nu\exp[-W_\nu t]), \tag{2}$$

where P_ν is the probability of the νth channel being open.

It was hypothesized that there is a continuum of relaxation channels with a small probability of any one of them being open. When this is the case, Eq. (2) reduces to the following expression:

$$l(t)=l_0\exp\left[-\sum_\nu P_\nu(1-\exp[-W_\nu t])\right],$$
$$=l_0\exp\left[-\int_0^\infty dW\,\rho_W(W)(1-e^{-Wt})\right], \tag{3}$$

where $\rho_W(W)$ denotes a weighted density of relaxation rates and is given by the equation

$$\rho_W(W)=\sum_\nu P_\nu\delta(W-W_\nu). \tag{4}$$

In this approach, stretched exponential decay is associated with singular behavior in the density of relaxation rates for the open channels as $W\to 0$, i.e., $\rho_W(W)\sim W^{-\alpha-1}$ leads to asymptotic stretched exponential relaxation characterized by the exponent α. Recently, a rigorous derivation of Eq. (3) was given by Vlad and Mackey [3], who showed that it is exact for a Poissonian distribution of independent channels.

The purpose of this paper is to outline a *dynamical* model of stretched exponential relaxation in which the channels are controlled by independent, thermally activated ''gates'' that open and close randomly with time. It is assumed that an ''open'' gate corresponds to the thermally excited state of the subsystem controlling the relaxation of the νth channel while the ''closed'' gate is associated with the subsystem ground state. In place of Eq. (1), one has an expression of the form

$$l(t)=l_0\left\langle \exp\left[-\sum_\nu \int_0^t w_\nu(t')dt'\right]\right\rangle, \quad (5)$$

where the angular brackets now refer to a thermal average. The symbol $w_\nu(t)$ denotes a time-dependent relaxation rate that assumes the value W_ν when the gate is open and 0 when it is closed. Since the channels are independent of one another, Eq. (5) can be written as a product over the various channels, viz.,

$$l(t)=l_0\prod_\nu \left\langle \exp\left[-\int_0^t w_\nu(t')dt'\right]\right\rangle. \quad (6)$$

The evaluation of the thermal average in Eq. (6) will be discussed in the following section.

II. MODEL CALCULATION

In this section, we outline a model calculation for the bracketed expression appearing in Eq. (6). Since the results apply to a single channel, we will drop the label ν for the time being. The approach we follow exploits the similarity between a situation where the relaxation rate fluctuates between the values W and 0 and an analogous situation occurring in magnetic resonance where the transition frequency fluctuates between two values [4,5]. The theory developed in Ref. [4] can be applied to the present situation, the only modification being the use of an imaginary frequency to represent the relaxation rate. The resulting expression for $\langle\exp[\ ]\rangle$ assumes the form

$$\left\langle \exp\left[-\int_0^t w(t')dt'\right]\right\rangle = \mathbf{P}\cdot\exp[-\Omega t]\mathbf{U}, \quad (7)$$

where $\mathbf{P}$ is a row vector with elements P and $1-P$, P denoting the probability the gate is open, and $\mathbf{U}$ is a column vector with both elements equal to 1. The 2×2 matrix Ω is defined in terms of the unit matrix $\mathbf{1}$, and the Pauli spin matrices σ_x, σ_y, and σ_z by means of the equation [5]

$$\Omega=(R+\tfrac{1}{2}W)\mathbf{1}-R\sigma_x-i\varepsilon\sigma_y+(\varepsilon+\tfrac{1}{2}W)\sigma_2, \quad (8)$$

where W denotes the relaxation rate associated with the channel in question. The symbols R and ε are related to the *gate* transition rates, R_{oc}, the transition rate from the "open" or excited state to the "closed" or ground state, and R_{co}, the transition rate from the closed state to the open state, through the equations

$$R=\tfrac{1}{2}(R_{oc}+R_{co}), \quad (9)$$

and

$$\varepsilon=\tfrac{1}{2}(R_{oc}-R_{co}). \quad (10)$$

It should be noted that for systems in thermal equilibrium, the two transition rates are related by a detailed balance equation, which takes the form

$$PR_{oc}=(1-P)R_{co}. \quad (11)$$

It is convenient to rewrite $\exp[-\Omega t]$ in terms of a complex unit vector $\mathbf{n}$ defined by

$$\mathbf{n}=(R,i\varepsilon,-(\varepsilon+\tfrac{1}{2}W))/C, \quad (12)$$

where C, a normalizing factor, is given by

$$C=[R^2+(\varepsilon+\tfrac{1}{2}W)^2-\varepsilon^2]^{1/2}. \quad (13)$$

The expression $\exp[-\Omega t]$ takes the form

$$\exp[-\Omega t]=\exp[-(R+\tfrac{1}{2}W)t]\exp[C\mathbf{n}\cdot\boldsymbol{\sigma}t]. \quad (14)$$

Using a standard identity for the Pauli matrices [5], the factor $\exp[C\mathbf{n}\cdot\boldsymbol{\sigma}t]$ becomes

$$\exp[C\mathbf{n}\cdot\boldsymbol{\sigma}t]=\cosh(Ct)+\mathbf{n}\cdot\boldsymbol{\sigma}\sinh(Ct). \quad (15)$$

Inserting Eq. (15) into Eq. (7) leads to the result

$$\left\langle \exp\left[-\int_0^t w(t')dt'\right]\right\rangle = e^{-[R+(1/2)W]t}\{\cosh(Ct) + C^{-1}[R+(\tfrac{1}{2}-P)W]\sinh(Ct)\}. \quad (16)$$

Equation (16) is seen to reproduce the expected behavior in the limits $W=0$, in which case $C=R$ and the right-hand side reduces to 1, and $R=\varepsilon=0$, in which case $C=\frac{1}{2}W$ and the right-hand side reduces to $1-P+P\exp[-Wt]$, corresponding to the static limit discussed in the Introduction. As will be shown in the following section, stretched exponential behavior is associated with situations where there is a continuum of channels for which $P\ll1$.

III. STRETCHED EXPONENTIAL RELAXATION

As in the static model, stretched exponential relaxation can arise when there is a continuum of relaxation channels where the probability of any single channel being open is much less than 1. As a starting point in the analysis, we evaluate the right-hand side of Eq. (16) by using the detailed balance equation to express $\mathbf{n}$ and C in terms of R_{oc} and P, and then expand the expressions to first order in P. The resulting equation takes the form

$$\left\langle \exp\left[-\int_0^t w(t')dt'\right]\right\rangle = 1-W^2(R_{oc}+W)^{-2}P + W^2(R_{oc}+W)^{-2}P \times\exp[-(W+R_{oc})t], \quad (17)$$

having approximated C by its zeroth-order term, $\frac{1}{2}(W+R_{oc})$, in the arguments of the hyperbolic functions.

Equation (17) is similar to the expression in parentheses on the right-hand side of Eq. (2), except that in place of P and W, there appear *renormalized* probabilities and transition rates defined by

$$P^{Re}=W^2(R_0+W)^{-2}P \quad (18)$$

and

$$W^{Re}=(1+R_0/W)W. \quad (19)$$

Here we have made use of the assumption that $P \ll 1$ and replaced R_{oc} by its zero-temperature limit, R_0. Since the right-hand side of Eq. (17) is similar to the factor in parentheses on the right-hand side of Eq. (2), the resulting expression for $l(t)$, which is the counterpart of Eq. (3), has the form

$$l(t) = l_0 \exp\left(-\sum_\nu W_\nu^2 (R_{0\nu} + W_\nu)^{-2} P_\nu \times (1 - \exp[-W_\nu t - R_{0\nu} t]) \right). \tag{20}$$

Following Ref. [3], we can obtain the conditions for stretched exponential relaxation from the time derivative of the argument of the first exponential in Eq. (20). Matching the first derivative to the first derivative of t^α, we obtain the relation

$$\alpha t^{\alpha-1} \sim \sum_\nu W_\nu^2 (W_\nu + R_{0\nu})^{-1} P_\nu \exp[-W_\nu t - R_{0\nu} t]. \tag{21}$$

We introduce the joint distribution, $\rho_{WR}(W,R_0)$ for the relaxation rates and transition rates of the open channels by means of the equation

$$\rho_{WR}(W,R_0) = \sum_\nu P_\nu \delta(W - W_\nu) \delta(R_0 - R_{0\nu}), \tag{22}$$

so that Eq. (21) can be written

$$\alpha t^{\alpha-1} \sim \int_0^\infty \int_0^\infty dW\, dR_0 W^2 (W + R_0)^{-1} \rho_{WR}(W,R_0) \times \exp[-Wt - R_0 t]. \tag{23}$$

In our model, asymptotic stretched exponential relaxation reflects scaling behavior of $\rho_{WR}(W,R_0)$ near the origin. This can be seen by introducing the dimensionless variables $x = Wt$ and $y = R_0 t$. The function $\rho_{WR}(W,R_0)$ then becomes a function of the ratios x/t and y/t. The scaling behavior that is postulated is of the form

$$\rho_{WR}(x/t, y/t) \sim t^\beta g(x,y), \quad t \to \infty, \tag{24}$$

i.e., in the limit of small arguments, $\rho_{WR}(W,R_0)$ is a homogeneous function of degree $-\beta$. Using Eq. (24) in Eq. (23), we find that the right-hand side of this equation varies as $t^{\beta-3}$, from which we infer that $\alpha = \beta - 2$. Since we have $0 < \alpha < 1$ for stretched exponential behavior, β must satisfy $2 < \beta < 3$. We postpone discussion of this result to the following section.

IV. DISCUSSION

In this paper, we have outlined a dynamical model for the asymptotic stretched exponential relaxation of macroscopic parameters in solids. The basic assumption was that the relaxation took place simultaneously through a large number of channels that were controlled by gates. An open gate corresponded to a thermally excited state of the subsystem controlling that channel, while the closed gate was identified with the subsystem ground state. The contribution of the νth channel to the overall relaxation was set by the relaxation rate associated with the channel W_ν, the transition rates for closing and opening the gate, $R_{oc\nu}$ and $R_{co\nu}$, and the equilibrium probability that the gate would be in an open state P_ν, with the latter three parameters being related to one another by a detailed balance equation.

Stretched exponential relaxation arose in a situation where $P_\nu \ll 1$ (corresponding to an activation energy $\gg kT$). A critical condition was that $\rho_{WR}(W,R_0)$, the joint distribution of relaxation and transition rates for the open channels, had the scaling behavior displayed in Eq. (24), with $2 < \beta < 3$. It should be noted that since Eq. (23) is a two-dimensional Laplace transform, one can also employ various Tauberian theorems to characterize the asymptotic behavior of $\rho_{WR}(W,R_0)$ in more precise terms [6].

Although the model considered is probably too crude to be applicable in detail to any particular stretched exponential relaxation process, the essential features of relaxation occurring in parallel through a large number of channels and the presence of the thermal disorder (or, in the case of the model discussed in Ref. [2] static disorder) accompanied by scaling behavior in the joint distribution of single-channel relaxation and transition rates, may very well be characteristic features of many stretched exponential processes.

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[6] For example, by making the variable change $R_0 \to x = W + R_0$ in the integral in Eq. (23), $t^{\alpha-1}$ is proportional to the one-dimensional Laplace transform of the function $f(x) = x^{-1} \int_0^x dW\, W^2\, \rho_{WR}(W, x - W)$. With the aid of a Tauberian theorem, it is readily established that $f(x) \sim x^{-\alpha}$, as $x \to 0$.