

## Patterns of relaxation in disordered materials

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We analyze several nonexponential decay laws of current interest and point out their interrelations. Owing to bounds on measurement times and, hence, on the monitored relaxation, several descriptions of the decay are possible in which the maximum and minimum relaxation rates play a major role.

## I. INTRODUCTION

In disordered systems many processes of interest, such as electron and hole transport and recombination, energy transfer, and hole burning, display long-time tails.<sup>1-5</sup> Thus the corresponding decay forms deviate strongly from the exponential behavior characteristic for a well-defined relaxation rate. In a recent publication<sup>5</sup> a logarithmic time dependence was found to describe well the recovery dynamics of photochemically hole-burnt systems. This decay law is quite slow, and is, *vide infra*, intermediate between the more familiar nonexponential decays, such as the stretched exponential of Kohlrausch,<sup>6</sup> and Williams and Watts<sup>7</sup> or the algebraic decay forms typical for charge-recombination in semiconductors.<sup>8,9</sup> It was also pointed out by Queisser that a logarithmic decay may be very well used to analyze data pertaining to the relaxation of photoconductance near semiconductor interfaces, data which were formerly fitted using a Williams-Watts form.<sup>10</sup> It thus becomes important to consider the interrelations between the distinct analytical expressions. In this work we compare the various decay forms, and show that for slow decays the distinctions are not clear cut. A major role in determining the relaxation behavior is played by the maximum and minimum decay rates of the system considered: These rates enter very naturally in the analysis which uses the logarithmic expression.

## II. DECAY LAWS AND RATE DISPERSION

We start from usual forms of model decay laws, as they appear in the study of relaxation in disordered systems. Listing them in the order of increasingly slower decay, one has the following: (a) the Kohlrausch<sup>6</sup> or Williams and Watts<sup>7</sup> stretched exponential

$$\phi(t) = \exp[-(t/\tau)^\alpha], \quad (0 < \alpha < 1, \quad t > \tau), \quad (1)$$

(b) the exponential-logarithmic form of Inokuti and Hirayama, and Scher, Lax, Montrol, and Blumen,<sup>11-14</sup>

$$\phi(t) = \exp[-B \ln^\beta(t/\tau)], \quad (\beta \geq 1, \quad t > \tau), \quad (2)$$

and (c) the algebraic decay<sup>8,9,12,13</sup>

$$\phi(t) \sim (t/\tau)^{-\gamma}; \quad (\gamma > 0, \quad t > \tau). \quad (3)$$

Form (a) has been extensively discussed by Ngai,<sup>3</sup> who

pointed out that it is obeyed for wide classes of materials. Equation (1) is readily derivable by assuming a distribution of parallel rates.<sup>4,14</sup> Such a situation holds in the case of random distributions of active centers and microscopic distance-dependent interactions  $R(r)$ . From these the configurationally dependent relaxation rates  $R_K$  follow, with

$$R_K = \sum_{\mathbf{r}} \eta_K(\mathbf{r}) R(\mathbf{r}), \quad (4)$$

where the sum runs over available sites and  $\eta_K(\mathbf{r})$  is an index function, which equals one when the site is occupied by an active center and equals zero, otherwise. For short-ranged interactions, obviously, the major weight in Eq. (4) is carried by the nearest-neighbor center, say, at  $\mathbf{r}_{NN}$ , and thus  $R_K \approx R(\mathbf{r}_{NN})$ . One may, however, perform all averages exactly,<sup>14,15</sup> then for  $R(r) \sim r^{-s}$  Eq. (1) follows,<sup>16</sup> whereas for  $R(r) \sim \exp(-ar)$  one is led to Eq. (2).<sup>11,12,15</sup> Furthermore, concerning form (c), Scher and Lax<sup>12</sup> have demonstrated that over a quite large range of times Eq. (2), with  $\beta=3$ , may be approximated by decays of algebraic form, Eq. (3). This holds then, *a fortiori*, for  $\beta < 3$ , since for  $\beta=1$  the two forms (2) and (3) become absolutely equivalent, with  $B=\gamma$ .

A point which has to be stressed, is that Eqs. (1)–(3) are not suitable at very short times. This fact is transparent from their derivation,<sup>14</sup> and is evident by inspection of Eqs. (2) and (3). Whereas Eq. (1) is still well behaved at  $t=0$ , Eq. (2) is not defined for  $t < \tau$  and Eq. (3) diverges for  $t \rightarrow 0^+$ . Here we encounter already the requirement of a cutoff at short times (here incorporated in the equation as  $\tau$ ), i.e., the existence of a maximum relaxation rate  $R_{\max}$ .

An example in which a *minimum* relaxation rate  $R_{\min}$ , also plays a dominant role is the logarithmic relaxation pattern:

$$\phi(t) = 1 - D \ln(t/\tau). \quad (5)$$

In Ref. 5 this decay law was derived using general arguments concerning the distribution  $P(R)$  of rate parameters  $R$  per unit energy interval, as widely used in the physics of amorphous solids:<sup>17,18</sup>

$$P(R) \sim R^{-1} (1 - R/R_{\max})^{-1/2}, \quad (6)$$

where  $R_{\max}$  is weakly energy dependent. The experimental basis for the distribution of Eq. (6) are results for the specific heats of glassy materials.<sup>19</sup> The singularity at  $R_{\max}$  in the above distribution obtains for symmetric potentials;

in other cases it may be absent. For  $R \ll R_{\max}$  it can be safely neglected anyway, and thus, one has

$$P(R) dR \sim dR/R \quad (7)$$

Equation (7) simply states that  $R(\lambda) \sim \exp(-\lambda)$ , where the parameter  $\lambda$  is *homogeneously* distributed. Such a distribution leads to Eq. (2), as stated above for  $\lambda = ar$ . (Another, mathematically similar example is the model considered by Queisser.) Hence, with  $\beta = 1$ , one gets from Eq. (2)

$$\phi(t) = \exp[-B \ln(t/\tau)] \approx 1 - B \ln(t/\tau) \quad (8)$$

where the expansion holds for times such as  $\ln(t/\tau) \ll B^{-1}$ . Notice, however, that because of the logarithmic form of this condition, the range of times  $t$  for which the approximation holds is very large for small  $B$  values.

Therefore Eqs. (2) and (5) can be related by setting  $\beta = 1$  and  $B = D$  in Eq. (2). The relation, however, cannot hold for exceedingly long times, since for  $t > t_{\max} \equiv e^{(1/D)\tau}$  Eq. (5) becomes negative. This time-domain restriction is met by the physical requirement of a minimum relaxation rate  $R_{\min}$ . Setting  $R_{\min} = t_{\max}^{-1}$  and  $R_{\max} = \tau^{-1}$  one can now express  $D$  as given in Ref. 5:

$$D = [\ln(R_{\max}/R_{\min})]^{-1} \quad (9)$$

The importance of Eq. (9) resides in the fact that the parameter  $D$  of Eq. (5), or the parameter  $B$  in Eq. (2) may now be envisaged as arising from natural limits on the distribution of rates  $P(R)$ . Furthermore, Eq. (8) may be rewritten as

$$\phi(t) = (t/\tau)^{-B} \approx 1 - B \ln(t/\tau) \quad (10)$$

which, by setting  $\gamma = B$  in Eq. (3), allows us to express also  $\gamma$  via  $\gamma = B = D$  in terms of the quotient  $R_{\max}/R_{\min}$  as in Eq. (9).

These results show that Eqs. (2), (3), and (5) are equivalent mathematical expressions in the time range  $t_{\min} \ll t \ll t_{\max}$ . Notice, however, that for small  $D$  (or  $B$ ,

or  $\gamma$ ) values this range is huge: for  $D = 0.02$  one has

$$t_{\max}/t_{\min} = t_{\max}/\tau = e^{50} \approx 5 \times 10^{21}$$

Furthermore, for such small values even Eq. (1) may be used as an approximation to Eq. (5) (or vice versa), a fact already noticed by Queisser.<sup>10</sup> For small  $\alpha$

$$(t/\tau)^\alpha = \exp[\alpha \ln(t/\tau)] \approx 1 + \alpha \ln(t/\tau) \quad (11)$$

which inserted into Eq. (1) and allowing for the cutoff at  $\tau$  turns it with  $\alpha = B$  into Eq. (2). Since in the experiment of Ref. 10 one has  $\alpha = 0.035$ , all forms Eqs. (1)–(5) can well describe the experimental findings over some 12 orders of magnitude in the time domain.

### III. CONCLUSIONS

In this work we have shown that depending on the experimental conditions and on the distribution of relaxation rates, mathematically distinct decay forms may describe well the same set of data. This finding is due to the fact that for slow decays deviations inherent in the analytical forms appear well outside the time (or, equivalently, rate) regime which is monitored experimentally. Significant deviations show up only when the dynamical range of the decay (and not only the time range) is large. From a heuristic point of view, analyses of the data in terms of logarithmic laws<sup>5,10,20</sup> are very informative since they can provide information on natural bounds of the system.

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