Stretched-exponential relaxation modeled without invoking statistical distributions

Chris G. Van de Walle
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304

(Received 7 November 1995)

Relaxation phenomena in disordered systems are often described by stretched exponentials; such behavior has traditionally been explained by invoking statistical distributions. In hydrogenated amorphous silicon, the relaxation has been associated with dispersive diffusion of hydrogen, related to a distribution of energies for trap states and barrier heights. Here we show that invoking such energy distributions is unnecessary; a treatment of hydrogen motion which includes retrapping leads to a functional form of the decay curve which closely resembles a stretched exponential, and provides an excellent fit to experimental data. The implications of the new microscopic model are discussed.

Stretched-exponential relaxation,[1] which is described by a time dependence

$$X=X_0\exp[-(t/\tau)^{\beta}], \qquad (1)$$

is commonly observed in disordered systems. Traditionally this type of relaxation has been modeled by invoking statistical distributions.[2,3] In hydrogenated amorphous Si (a-Si:H), for instance, the relaxation has been attributed to the motion of hydrogen,[4] which was found to exhibit time-dependent diffusion. The dispersive diffusion was associated with the presence of a distribution of activation energies for motion in the amorphous network (as opposed to a single activation energy in a crystal). While this phenomenological description is consistent with the observations, to our knowledge no direct evidence exists to support the assumptions about the microscopics of the process.

In this paper we offer an alternative, simple explanation for the observed relaxation. We describe the approach in the context of hydrogenated amorphous silicon, but its applicability may be more general. We will show that our model provides a fit to experimental data which is at least as good as the traditional stretched exponential [Eq. (1)]. We thus conclude that it is *not necessary* to invoke statistical distibutions to explain stretched-exponential decay.

Relaxation processes in a-Si:H are governed by hydrogen being released from *trap* sites.[4] An initial high concentration of H in these traps may be generated, for instance, by a quenching process. While hydrogen resides in the traps, certain measurable quantities (for instance, the spin density) have an enhanced value. As H is released from the traps, this value decays. It was observed early on that this decay could not be described by a regular exponential function; however, the stretched-exponential form [Eq. (1)] provides a good fit. The hydrogen that is released from the traps returns to a lower-energy state, which we label the *reservoir*. In the traditional explanation of stretched-exponential behavior, the functional form of the decay has been attributed to the fact that, in an amorphous material, the energies of the trap states and of the reservoir are not sharp energy levels, but exhibit a distribution. While the existence of such energy distributions is plausible in principle, to our knowledge no experimental or theoretical information is available to quantify the concept.

In the model proposed in this paper, there is no need to invoke a distribution of energy levels (although broadening of levels may still be present). We assume that there is a single energy level corresponding to the trap state (denoted T), and a single (lower-lying) level corresponding to the reservoir (denoted R) (see Fig. 1). In order to describe the decay, it is important to consider the microscopic aspects of the release process. Figure 1 schematically displays energy as a function of the spatial coordinate of the H atom. A potential well around a trapped state is shown, and also a potential well around a reservoir state. In addition, the figure illustrates that after the H escapes from the trapped state, it has to move some distance through the material before it finds a reservoir state, where it gets caught. This migration through the crystal proceeds through interstitial sites (labeled I), with intervening saddle points. The interstitial diffusion proceeds with a migration barrier in the range of 0.2–0.5 eV,[5] and is therefore not a rate-limiting step.

Previous considerations of decay processes have addressed the transition between T states and R states, without regard for the intermediate interstitial states; however, such a treatment neglects an important aspect of the decay process, namely the fact that a hydrogen that is released from a trap can be *retrapped* at the same or at another trap site. We show here that by writing down the reactions describing the trapping and release of hydrogen, and after some approximations, one arrives at a functional form which contains only

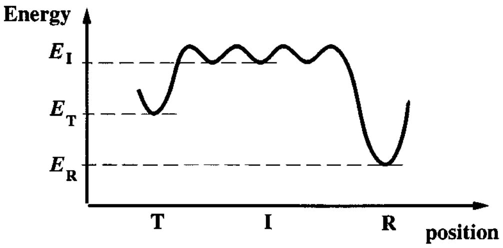

FIG. 1. Schematic diagram depicting energy as a function of position of hydrogen in the material, for various configurations of the impurity. As explained in the text, R refers to the ground state (''reservoir''), T to the trap state, and I to the interstitial hydrogen which diffuses through the crystal.

two parameters and turns out to behave much like the traditional stretched exponential. The difference, however, is that the parameters can now be directly associated with the rates of various microscopic processes, without having to make any assumptions about energy distributions. The quality of the fit will be illustrated with examples from the field of amorphous silicon. We stress, however, that the applicability of this model should not be limited to the specific case of amorphous silicon, or of hydrogen release and trapping.

The concentration of sites available for trapping hydrogen is labeled N_T, and the actual concentration of H atoms in these sites is denoted $[T]$. N_R and $[R]$ denote the corresponding quantities for the reservoir. $[I]$ stands for the number of H atoms in interstitial sites. The reaction describing the release and trapping of H at T sites is

$$\frac{d[T]}{dt} = -\nu_T[T] + \sigma_T[I](N_T - [T]), \tag{2}$$

where the first term represents the release of H from the traps, with a rate constant ν_T, and the second term describes trapping, with a capture parameter σ_T; $(N_T - [T])$ is the number of unoccupied trap sites.

Similarly, the reaction describing the release and trapping of hydrogen at the reservoir can be written as

$$\frac{d[R]}{dt} = -\nu_R[R] + \sigma_R[I](N_R - [R]). \tag{3}$$

Here we have assumed that the capture of hydrogen in a reservoir state is a unimolecular process; this is true, for instance, when the reservoir state corresponds to H atoms bound to Si dangling bonds. If the reservoir consisted of H_2 molecules, the trapping process would contain a quadratic term. The resulting equations would become slightly more complicated, but the qualitative conclusion (namely, that the functional form of the decay closely resembles a stretched exponential) remains unaltered.[6]

The total number of H atoms in the system is constant, of course

$$[T] + [I] + [R] = \mathrm{H}_{\mathrm{tot}}. \tag{4}$$

The basic equations (2), (3), and (4) are all we need to derive our conclusions. These conclusions are most easily observed if analytical solutions can be obtained, which is possible only if some simplifying assumptions are made. First we discuss two assumptions which will hold through the remainder of this paper.

Assumption I: The reaction described by Eq. (2) proceeds much faster than the reaction involving the reservoir [Eq. (3)]. On the time scale and for the temperatures of interest, dynamic equilibration between the $[T]$ and $[I]$ states is then obtained, and $d[T]/dt = 0$, leading to

$$[I] = \frac{\nu_T[T]}{\sigma_T(N_T - [T])}. \tag{5}$$

Assumption II: $[I] \ll [T]$ (as well as $[I] \ll [R]$). This assumption is well satisfied for the example under discussion, since isolated interstitial hydrogen has a low solubility (see Ref. 7).

Experimental observations consist of measuring a quantity which is related to the number of H atoms which have been excited out of the ground state (i.e., the reservoir). If we label the experimentally observed quantity X, then

$$X = [T] + [I] \approx [T]. \tag{6}$$

Note that, in the case where the reservoir consists of hydrogen atoms in Si-H bonds, X also corresponds to the change in the spin density due to the dangling bonds which are generated when H is excited out of Si-H bonds. Using assumption II and Eq. (6), Eq. (5) becomes

$$[I] = \frac{\nu_T X}{\sigma_T(N_T - X)}. \tag{7}$$

Equation (3) then leads to, using Eqs. (4), (6) and (7)

$$\frac{dX}{dt} = \nu_R(\mathrm{H}_{\mathrm{tot}} - X) - \sigma_R \frac{\nu_T X}{\sigma_T(N_T - X)}(N_R - \mathrm{H}_{\mathrm{tot}} + X). \tag{8}$$

We will come back to considering Eq. (8) in full later. A great deal of insight can be gained, however, by making some additional assumptions:

Assumption III: At the measurement temperature, no H atoms can escape from the reservoir. This situation may correspond to a quenching experiment, where the system is first heated to allow a measurable number of H atoms to escape from the reservoir and get trapped at T states, and then quenched to a lower temperature, at which no further escape from the reservoir is possible; the dynamics then consist of hydrogen being released from trap states, possibly being retrapped, and finally disappearing into the reservoir. Assumption III corresponds to neglecting the first term on the right-hand side in Eqs. (3) and (8). A further simplification can be introduced:

Assumption IV: $[R] \ll N_R$; i.e., the number of available sites in the reservoir is much larger than the number of H atoms.

Using assumptions III and IV, Eq. (8) becomes

$$\frac{dX}{dt} = -\sigma_R \frac{\nu_T X}{\sigma_T(N_T - X)} N_R = -r \frac{X}{N_T - X}, \tag{9}$$

where

$$r = \frac{\sigma_R N_R \nu_T}{\sigma_T}. \tag{10}$$

Thanks to our simplifying assumptions, we have arrived at a differential equation that can be integrated analytically. If we write (9) as

$$dt = -\frac{(N_T - X)}{rX} dX \tag{11}$$

and integrate both sides, we obtain

$$t = -\frac{N_T}{r}\ln\frac{X}{X_0} + \frac{X_0}{r}\left(\frac{X}{X_0} - 1\right) = -\tau'\ln\frac{X}{X_0} + \gamma\left(\frac{X}{X_0} - 1\right), \tag{12}$$

where we have chosen the initial conditions such that at $t = 0$, $X = X_0$, and introduced the notation

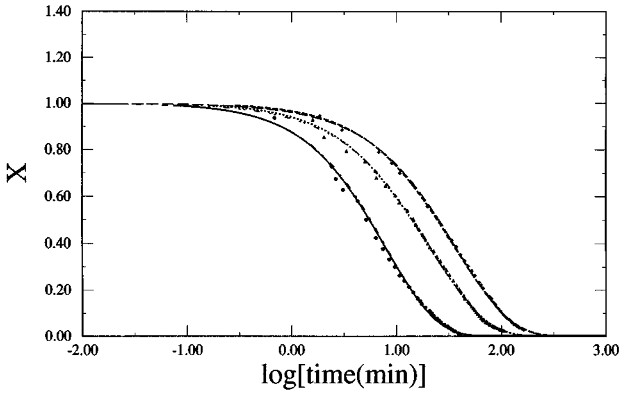

FIG. 2. Decay of the normalized light-induced dangling-bond density in *a*-Si:H for various temperatures (130, 140, and 160 °C, from right to left). Data points are from Ref. 8. Fits to stretched exponentials [Eq. (1)] are given by dashed lines. Fits to the functional form (12) are indicated by solid lines. The parameter values used in both types of fit are listed in Table I.

$$\tau' = \frac{N_T}{r} = \frac{N_T}{N_R}\frac{\sigma_T}{\sigma_R}\frac{1}{\nu_T}, \quad \gamma = \frac{X_0}{r}. \tag{13}$$

Note that these relationships imply that $\gamma/\tau' = X_0/N_T$; since $X_0 < N_T$, it follows that $\gamma < \tau'$. If $X_0 \ll N_T$, then $\gamma \ll \tau'$, and the decay curve will closely resemble a regular exponential; indeed, in the limit $\gamma = 0$ Eq. (12) reduces to a regular exponential. The deviation from the regular exponential thus occurs for cases where X_0 (and X) are of the order of N_T, i.e., if there is a significant population of the available trapping sites. The notation τ' is used to distinguish this time constant from the τ in the regular stretched exponential (1). For $\gamma \neq 0$, the presence of the additional term on the right-hand side of Eq. (12) leads to a steepening of the slope of the decay for t values smaller than γ, while the effect becomes negligible at large t, where the curve reduces to a regular exponential with time constant τ'. The deviation from a regular exponential for short times corresponds to a faster relaxation, caused by a suppression of retrapping occurring when a significant fraction of the trap states are filled.

At first sight, the functional form (12) seems distinctly different from the stretched exponential (1), which can also be written as

$$t = \tau\left[-\ln\frac{X}{X_0}\right]^{1/\beta}. \tag{14}$$

In spite of this difference, we find that the functional form (12) behaves remarkably similarly to a stretched exponential. This is best illustrated by using each of the two forms to fit the same set of experimental data, shown in Fig. 2. The data in question were taken from Ref. 8, where they were fitted with a stretched exponential [dashed lines, Eq. (1) or (14)]. The τ and β values obtained in Ref. 8 are listed in Table I. Figure 2 also shows how the data can be fitted with the functional form (12) (solid lines), with τ' and γ values also listed in Table I. To the naked eye, the fit is virtually indistinguishable from the one obtained with the stretched-exponential form. The quality of the fit is also confirmed by the very similar small values of χ^2 for both types of fit.

TABLE I. Fitting parameters for the fits displayed in Fig. 2.

Temperature	τ	β	τ'	γ
130 °C	42.3	0.81	68.4	41.8
140 °C	23.4	0.81	37.9	23.3
160 °C	7.72	0.87	10.8	4.92

The τ values obtained from the stretched-exponential fits for data at different temperatures were found to exhibit Arrhenius behavior, described by $\tau = \tau_0 \exp(E_A/kT)$. Reassuringly, the τ' values obtained from fitting with Eq. (12) can equally well be fitted in this fashion, leading to τ_0 and E_A values very similar to those obtained using the stretched-exponential model. Such fits produce τ_0 values in the range 10^{-7}–10^{-8} s, i.e., an unusually large prefactor. If the process consisted simply of the hydrogen being released from a trap by escaping over a barrier, one might expect the prefactor to be determined by a typical phonon frequency. In our model, the time constant τ' [Eq. (13)] includes other factors besides the release rate (ν_T). Indeed, $1/\nu_T$ is scaled by $N_T\sigma_T/N_R\sigma_R$, where $N_T\sigma_T$ can be interpreted as a total capture rate for trap states, and $N_R\sigma_R$ as a total capture rate for reservoir states, offering a natural explanation for why the prefactor can be substantially different from a typical phonon frequency.

The excellent fit observed in Fig. 2 is not an isolated instance. We have applied the procedure of fitting with Eq. (12) to a variety of data in the literature on amorphous[9] and polycrystalline[10] silicon, with very good results. In this literature, we have not yet encountered a case where Eq. (12) was unable to produce a fit that was at least as good as the stretched exponential. Our assumptions I–IV were made solely to enable obtaining an analytical solution [Eq. (12)]; a more general approach that avoids these assumptions would lead to an expression containing more parameters, which could only improve the quality of the fits.

The basic idea of including retrapping of hydrogen as an essential component of a relaxation process is not novel; for instance, it was applied by Zundel and Weber[11] in their analysis of the reactivation kinetics of passivated boron in silicon. However, to our knowledge, the notion of retrapping has not previously been invoked to explain relaxation behavior in disordered systems, and the resemblance of the resulting time dependence to a stretched exponential has not previously been pointed out.

It is tempting to think that because the plotted functions look so similar, there should be a direct relationship between the parameters τ and β on the one hand, and τ' and γ on the other. However, we have not been able to find such a relationship; linearization of the curves leads to distinctly different answers, depending on the point around which the linearization is performed. The approach we are proposing here is therefore not a simple transformation of the regular stretched exponential.

The real test of the validity of Eq. (12) to explain experimental observations should come from an inspection of the variations in the parameters corresponding to controlled changes in the experimental conditions. We already showed favorable results with respect to changes in temperature. An intriguing feature of the functional form (12) is that the parameter γ is proportional to X_0, which reflects the initial conditions. We have not yet been able to identify experimental data which provide sufficient detail to address this issue.

Another interesting aspect of our model should be highlighted, namely the behavior of the system in response to small deviations from equilibrium. In order to address near-equilibrium situations, we have to drop assumption III, and allow H atoms to escape from the reservoir, thereby establishing an equilibrium between hydrogen in reservoir and in trap states. Even if we still keep assumption IV, the resulting complication makes analytical solution of Eq. (8) difficult. However, it is straightforward to inspect the qualitative behavior when a small deviation from equilibrium is applied.[6] The equilibrium solution X_e is obtained by setting $dX/dt=0$. A small deviation is then introduced: $X=X_e+\delta$; by substituting this expression in Eq. (8) and using the fact that X_e sets the right-hand side of (8) equal to zero, a differential equation for δ is obtained, which turns out to be of the same form as Eq. (9) (with different parameters, of course); i.e., the relaxation of the system in response to a small deviation from equilibrium is described by the same ''stretched-exponential-like'' functional form that we examined previously. This type of behavior has been observed in conductivity measurements of doped a-Si:H after small thermal perturbations.[9] The fact that our model reproduces this behavior is significant; other models tend to reduce to a simple exponential decay when small perturbations from equilibrium are applied.

In summary, we propose a model for dispersive decay which does not invoke the usual assumption about statistical distributions leading to the conventional stretched exponential. The model is able to fit a variety of experimental data, and provides a physical explanation for the parameters extracted from the fit. We do not suggest that this model applies to *all* situations where stretched-exponential decay is observed; however, none of the other approaches that have been proposed to explain stretched-exponential behavior can claim universal applicability either.[3] While most of these other explanations invoke statistical distributions, the model described here shows that a statistical distribution is *not required* to obtain a stretched-exponential-like decay.

Thanks are due to M. Cohen, C. Herring, W. Jackson, C. Nebel, and R. Street for useful discussions.

---

[1] R. Kohlrausch, Ann. Phys. (Leipzig) **12**, 393 (1847); F. Kohlrausch, Pogg. Ann. Phys. **199**, 352 (1863).

[2] H. Scher, M. F. Schlesinger, and J. T. Bendler, Phys. Today **44** (1), 26 (1991).

[3] D. L. Huber, Phys. Rev. B **31**, 6070 (1985).

[4] J. Kakalios, R. A. Street, and W. B. Jackson, Phys. Rev. Lett. **59**, 1037 (1987).

[5] C. G. Van de Walle and R. A. Street, Phys. Rev. B **51**, 10 615 (1995).

[6] C. G. Van de Walle (unpublished).

[7] C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994).

[8] W. B. Jackson and J. Kakalios, Phys. Rev. B **37**, 1020 (1988).

[9] C. E. Nebel, R. A. Street, W. B. Jackson, and N. M. Johnson, Philos. Mag. B **69**, 291 (1994).

[10] N. H. Nickel, N. M. Johnson, and C. G. Van de Walle, Phys. Rev. Lett. **72**, 3393 (1994).

[11] T. Zundel and J. Weber, Phys. Rev. B **43**, 4361 (1991).