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Glass Relaxation Kinetics: Dynamic Activation Energy Assumption

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20. Abstract (Continued)

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Glass Relaxation Kinetics: Dynamic Activation Energy Assumption*

Abstract: The assumption was made that the activation energy of a relaxation process can change slightly (<4%) as the system relaxes. The empirical consequences of such an assumption are as follows: (a) The normally exponential decay function becomes more gradual or broadened in precisely the manner observed for glass and polymer relaxations; the well-known fractional-exponential expression for the response function $M(t) = \exp [-(t/\lambda)^b]$, where b is the fractional power of the ratio of elapsed time t to relaxation time λ and where $0 < b < 1$, is easily obtained. (b) A well-defined temperature dependence is predicted for the width parameter b , which is in excellent agreement with recent measurements on B_2O_3 glass. (c) Conventional finite-amplitude (nonlinear) correction terms can be introduced in a more unified manner than was previously possible. A simple physical justification for this time-dependent activation energy is that the structural units that relax later encounter a somewhat larger activation barrier than do the units that relax first.

INTRODUCTION

We can characterize the relaxational behavior of glass largely in terms of its not obeying simple viscoelastic theory. Typically, the decay function for glassy relaxation is not a simple exponential. Its temperature dependence does not follow Arrhenius behavior [1]. Further, for moderate perturbations, its relaxational response readily departs from linearity. Hence, we term its behavior as nonexponential, non-Arrhenius, and nonlinear. Presumably, these three features are interrelated, but they cannot be properly explained until the detailed molecularity of the glassy relaxation process is better understood. Lacking such a model for this process, we are left (for the most part) with only empirical descriptions to guide us in reducing data.

This report suggests a plausible explanation of the first of these characteristics: non-exponentiality. No adequate interpretation of this behavior has previously been reported. Instead, it is generally only loosely attributed to cooperative interaction among the various relaxing units of the glass (i.e., molecules) without further elaboration. This report offers a more specific, mathematical, description. Although the approach presented is largely phenomenological in origin, it can also be interpreted in terms of a simple physical model.

We do not attempt to account for either of the other two characteristics mentioned: non-Arrhenius and nonlinear behaviors. The existence of these two is, however, recognized in the mathematical formulations used.

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CONVENTIONAL DESCRIPTION

This section presents certain equations that are commonly used to represent glass relaxation data. It is included primarily as a vehicle for defining the parameters and terminology that will be used in later sections.

In relaxation studies, a system initially in equilibrium is suddenly disturbed by a change in some external parameter, such as temperature or pressure. As the system approaches its new equilibrium, the response of a physical property X of the system is monitored as a function of time t . This response may be written as

$$X(t) - X(\infty) = [X(0) - X(\infty)]M(t), \quad (1)$$

where $X(0)$ and $X(\infty)$ are the instantaneous and long-time values of X . The term $M(t)$ is called the response function. It is normalized to 1 at zero time, and to 0 at infinite time.

For the simplest type of relaxational process, the response function is an exponential,

$$M(t) = \exp \frac{-t}{\lambda^\circ} \quad (2)$$

where λ° is a constant, called the relaxation time. Equation (2), actually the integrated form of a more basic relationship, namely, the fractional rate of approach to equilibrium, is a constant:

$$-\frac{1}{M(t)} \frac{dM(t)}{dt} = \frac{1}{\lambda^\circ} \quad (3)$$

For such a simple process, the temperature dependence of relaxation time is typically expressible by an Arrhenius-type equation:

$$\lambda^\circ = A^\circ \exp \frac{E_a^\circ}{RT}, \quad (4)$$

where R is the gas constant, E_a° is the activation energy, and A° is a proportionality constant. Such a form for λ° arises when the rate-limiting step of the relaxation process is that of movement over an energy barrier.

Many real systems do obey such simple relationships, but glasses generally do not. The meanings of the terms nonexponential, non-Arrhenius, and nonlinear can now be clarified.

"Nonexponential" indicates that Eq. (2) does not apply. Specifically, although $M(t)$ can remain simply a function of t/λ° , its functional form must change more gradually with time than a simple exponential. In such cases, it is convenient to continue using the parameter λ° as a measure of gross relaxation time. We must therefore define λ° independently of its use in Eqs. (2) and (3) (which are not applicable in this case). It is experimentally useful to define it by the constraint,

$$\lambda^\circ = t$$

when

$$M(t) = \frac{1}{e}. \quad (5)$$

This definition is consistent with the use of λ° in Eq. (3).

“Non-Arrhenius” indicates that the temperature dependence of λ° does not obey Eq. (4) over the entire temperature range used. Equation (4) can be retained, however, if we allow E_a° and A° to be temperature dependent. This variation is permissible because E_a° and A° change much more slowly with temperature than does λ° . An experimentally meaningful evaluation of E_a° then requires only the measurement of λ° at two closely spaced temperatures, T_1 and T_2 :

$$E_a^\circ \equiv R \frac{\ln \lambda_1^\circ - \ln \lambda_2^\circ}{1/T_2 - 1/T_1}. \quad (6)$$

Finally, “nonlinear” indicates that $M(t)$ in Eq. (2) is not just a function of t/λ° , but rather contains additional terms related to the actual magnitude of the deviation from equilibrium. These nonlinearities are poorly understood and rarely studied. They become significant only when appreciable perturbations from equilibrium occur.

PRESENT APPROACH

There are two often-used approaches toward reducing linear, nonexponential glassy relaxation data. Both are entirely phenomenological, and both use modifications of Eq. (2): The first, called the fractional exponential approach, simply raises t/λ° in Eq. (2) to a power, b , where $b = 1$ for a simple relaxational process, and $0 < b < 1$ for the more distributed glassy relaxational process. Although this formulation is simple to use and accurately fits an extensive body of data, it has no apparent physical interpretation. The second approach, called the relaxation spectrum model, expresses $M(t)$ as the sum of a large (or infinite) number of simple exponential t/λ terms, each with an associated weighting factor. The result is simply a mathematical transform, which can be quite useful in certain applications. In addition, although it is phenomenological in origin, it nonetheless does have a plausible physical interpretation: a distribution of molecular environments can yield a distribution of simple exponential relaxation processes. This formulation, however, is very unwieldy to use in reducing experimental data, because the least-squares evaluation of a large number of fitting parameters requires considerable computational effort.

This report uses a quite different approach. Here, *we allow activation energy to change slightly with time during the course of the relaxation process. This time-dependent activation energy will introduce a time dependence in the relaxation time, as well.*

Specifically, in a manner analogous to Eq. (3), we define a time-dependent relaxation time, $\lambda(t)$, as the instantaneous value of the fractional rate of approach to equilibrium:

$$\frac{1}{\lambda(t)} \equiv - \frac{1}{M(t)} \frac{dM(t)}{dt}. \quad (7)$$

We then define a time-dependent activation energy in terms of $\lambda(t)$ in a manner analogous to that of Eq. (4):

$$\lambda(t) = A \exp\left(\frac{E_a(t)}{RT}\right). \quad (8)$$

Here A now can be temperature, but not time, dependent. It is only a proportionality constant, however, and is generally eliminated from final expressions.

Together, Eqs. (7) and (8) allow us to transform the observed time dependence of $M(t)$ into a time dependence of $E_a(t)$. It will be shown that this exchange can be both simple and advantageous.

The use of a time-dependent relaxation time is not new. In expressions for relaxation time, Tool [2], and later Narayanaswamy [3], included a fictive temperature term, which is implicitly time dependent. In analyzing their experimental data, Sharonov and Vol'kenshtein noticed that graphs of $M(t)$ vs $\ln \lambda(t)$ appear linear [4, 5]. This observation is also apparent in the work of Goldstein and Nakonecznyj [6]. Even so, the concept of a time-dependent relaxation time (or activation energy) has not previously been pursued or exploited.

To include a time dependence in activation energy, we can expand $E_a(t)$ as a polynomial in terms of some as yet undefined reaction variable $x(t)$. Thus,

$$E_a(t) = E'_a [1 + ax(t) + \dots]. \quad (9)$$

In this equation, E'_a is an adjustable parameter, whose value can be related to the experimentally meaningful parameter E_a° by this convenient constraint:

$$\text{when } t=\lambda^\circ, \text{ let } E_a(t) = E_a^\circ. \quad (10)$$

This permissible constraint is a natural choice, considering that E_a° is defined in terms of λ° (Eq. 6). Equation (9) can then be better expressed as

$$E_a(t) = E_a^\circ \frac{[1 + ax(t) + \dots]}{[1 + ax(\lambda^\circ) + \dots]}. \quad (11)$$

Presumably any reasonable form of $M(t)$ can be described in this manner, with the use of any reasonable choice of reaction variable $x(t)$, so long as enough terms are retained in the polynomial expansion. For practical use, however, it is necessary that we use a reaction variable such that an adequate description is provided when only linear terms are retained:

$$E_a(t) = E_a^\circ \frac{[1 + ax(t)]}{[1 + ax(\lambda^\circ)]}. \quad (12)$$

We then have only one width parameter, a , describing the departure from simple exponential behavior.

In each of the following two sections, a particular choice of $x(t)$ is considered. The following section investigates the choice $x(t) = \ln(t/\lambda^\circ)$. With this choice, the equations

presented are found to reduce to the familiar fractional-exponential form for $M(t)$. Next, the choice $x(t) = M(t)$ is studied. Although the resulting equations are more complicated, nonetheless satisfactory data agreement is obtained. This choice of variable has the advantage that $M(t)$ has a physical meaning (extent of relaxation) aside from its use as a reaction coordinate.

REACTION VARIABLE $\ln(t/\lambda^\circ)$

A particularly convenient choice for $x(t)$ is $\ln(t/\lambda^\circ)$. This reaction variable is familiar [1]. For example, when depicting the measured time dependence of the decay function, one generally plots $M(t)$ vs $\ln(t/\lambda^\circ)$ (or $\log_{10}(t/\lambda^\circ)$), as in Fig. 1. Assuming thermorheological simplicity, such a graph allows data, collected under differing experimental conditions, to fall along the same smooth curve. Thus the reaction variable $\ln(t/\lambda^\circ)$ is specific only to the shape of the decay function, and is independent of the location of the relaxation along the time axis.

With $\ln t/\lambda^\circ$ as the choice of reaction variable, the formulation presented readily reduces to

$$M(t) = \exp \left[-\left(\frac{t}{\lambda^\circ}\right)^b \right] \tag{13}$$

where

$$b \equiv 1 - \frac{a_f E_a^\circ}{RT} \tag{14}$$

and a_f is parameter a of Eq. (12). The details of this derivation are given in Appendix A.

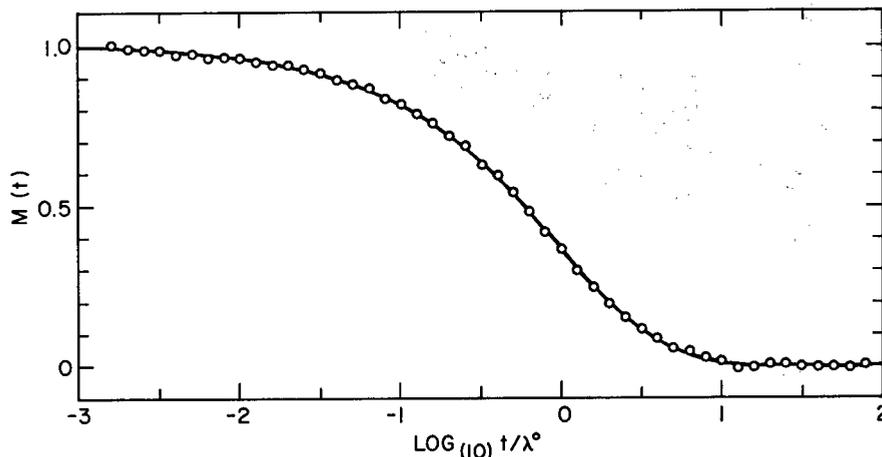


Fig. 1 — Relaxational decay, $M(t)$ vs t (where $M(t)$ is the response function), for B_2O_3 glass, fit to the fractional-exponential equation. Data (circles) are from pressure-jump volume relaxation study of Ref. 1.

Equation (13) is the familiar fractional-exponential equation. It is well known that this equation provides an excellent description of an extensive body of glass relaxation data. The solid curve in Fig. 1, for example, was constructed with the use of a least-squares fit to Eq. (13). Hence, for the first time, we are able to suggest a plausible origin for the fractional exponential equation.

Accompanying this result is a predicted dependence of b on temperature (Eq. (14)) which includes no assignable parameters. From one determination of b at any one temperature, values of b can be calculated over the entire range of temperatures for which E_a° is known. No previous formulation allows such a prediction. Hence, we can devise a test of the empirical usefulness of the derivation presented here.

Bucaro et al. recently measured the temperature dependence of the width parameter b for B_2O_3 glass at temperatures near and within the glass transformation region [7]. Their data are shown here as Fig. 2. Data points indicated by squares are from light-scattering correlation, and those shown as circles are from pressure-jump, volume-relaxation measurements. The relaxation is seen to narrow ($b \rightarrow 1$) as temperature is increased.

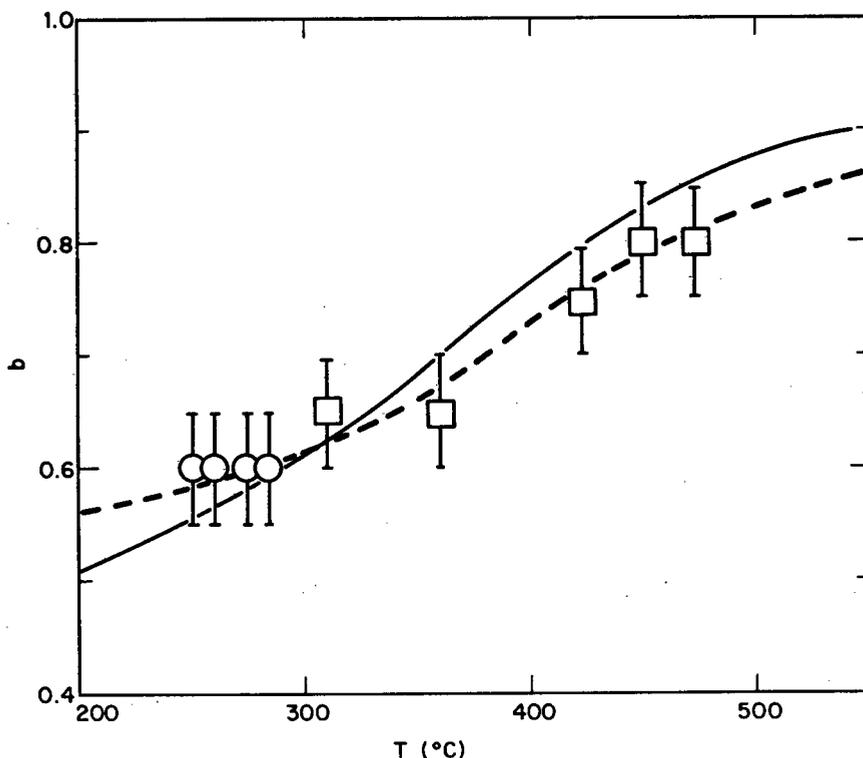


Fig. 2 — Temperature dependence of width parameter b for B_2O_3 glass. Solid line is fractional exponential; dashed line is for the form where the reaction variable is the response function. Squares represent data from light-scattering correlation spectroscopy [7]; circles are from pressure-jump volume relaxation [1].

To use Eq. (14) one must know the activation energy of this process over the temperature range of interest. Such data is available, and is shown in Fig. 3. Here, the circles and squares are evaluated as for Fig. 2. The triangles are from earlier ultrasonic data [8]. All relaxation times used to evaluate E_a° are compressional, and the shape of the curve is drawn to be also qualitatively consistent with the better-established temperature dependence of E_a° for shear [9].

With E_a° and b known at only one temperature (e.g., 300°C), a_f can be evaluated from Eq. (14). Values of b can then be predicted at any temperature for which E_a° is known. The continuous line in Fig. 2 shows the temperature dependence predicted by this equation (with $a_f = 0.0054$).

The predicted temperature dependence of b is seen to be in good agreement with these data. Unfortunately, suitable data on other glasses are not available over a sufficient temperature range to allow additional testing of the applicability of Eq. (14). Regardless, for the one glass (B_2O_3) where sufficient data are available, the approach used here accurately predicts the temperature dependence of the relaxation width, without introducing any additional fitting parameters. We conclude, therefore, that this approach provides a phenomenologically more complete description of the glassy relaxation process than those previously available.

REACTION VARIABLE $M(t)$

Another obvious reaction variable is the decay function $M(t)$, itself. With this choice, the formulations presented are found (Appendix B) to reduce to

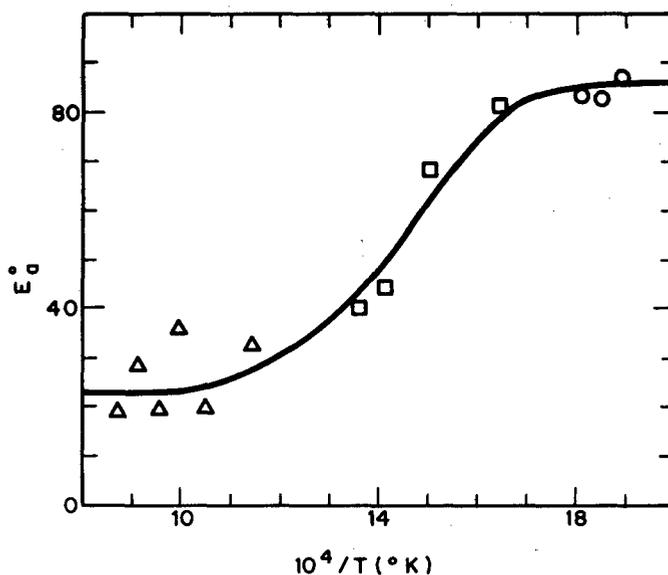


Fig. 3 — Temperature dependence of activation energy E_a° for B_2O_3 glass. Solid line shows trend. Squares and circles are as in Fig. 2. Triangles represent data from ultrasonic spectroscopy [2].

$$\frac{t}{\lambda^{\circ}} = \frac{Ei(m) - Ei(mM(t))}{Ei(m) - Ei(m/e)} \quad (15)$$

where

$$m \equiv \frac{a_m}{1 + a_m/e} \frac{E_a^{\circ}}{RT} \quad (16)$$

Here Ei is the exponential integral [10], which can be evaluated from tables or from an infinite series expansion (Appendix B), and a_m is parameter a of Eq. (12) whose value is specific to this choice of reaction variable.

Note that the values of a_m and m are both negative, because the reaction variable $M(t)$ decreases as the relaxation proceeds. Also, note that Eq. (15) represents relaxational decay with use of t/λ° as a function of $M(t)$, rather than the more usual representation, $M(t)$ as a function of t/λ° . This difference is immaterial.

A relationship somewhat similar to this one (Eq. (B2) in Appendix B) was proposed by Sharonov and Vol'kenshtein [4, 5], who noted that graphs of $\ln \lambda(t)$ vs $M(t)$ appear linear. This behavior, however, is not a good test of the applicability of Eq. (15), because when the incremental derivative term of $\lambda(t)$ (Eq. 7) is evaluated, the cumulative contribution of small errors is ignored.

A much better test is to compare experimental data directly with the shape of the decay function (Eq. (15)). The data shown in Fig. 1 were, therefore, fit to Eq. (15) with $m = -1.75$. As shown in Fig. 4, the quality of the fit is excellent. The calculated time dependence is shown by the line, which in all cases lies within the uncertainty limits of the data (± 0.02). Hence it is concluded that Eq. (15) adequately represents this quite typical set of relaxation data.

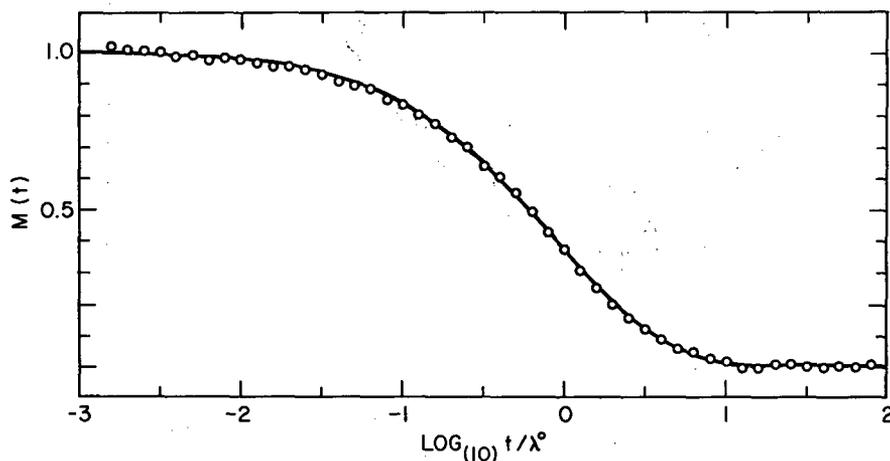


Fig. 4 — Relaxational decay, $M(t)$ vs time t (where $M(t)$ is the response function), of B_2O_3 glass, fit to Eq. (15) (form $x = M(t)$ where x is the reaction variable)

Because m and b (Eqs. (16) and (14), respectively) are both independent width parameters, some correspondence exists between their values. To determine this correspondence in an experimentally meaningful manner, we generated an idealized set of $M(t)$ data with selected values of m in Eq. (15). These data were then fit to the fractional-exponential equation, Eq. (13). The values of b thus determined are shown in Fig. 5. This figure can henceforth be used to estimate the value of one of these parameters (b or m) from an evaluation of the other.

Because such a correspondence exists, the temperature dependence of b can also be predicted with this present form ($x = M(t)$). In the same manner as before, Eq. (16) allows us to calculate values of m over the temperature range of interest. Corresponding b values can then be estimated from Fig. 5. The temperature dependence of b thus predicted is shown by the dashed line in Fig. 2. The agreement with the data is again excellent—well within experimental error. We conclude, therefore, that the choice of $x(t) = M(t)$ also provides an excellent fit to these experimental data.

It might be noted that the value of a_m found for B_2O_3 glass is quite similar to that calculated for other oxide glasses. Thus, using the B_2O_3 value ($a_m = -0.0355$), we calculate $b = 0.51$ for soda-lime glass at $510^\circ C$ (experimental $b = 0.54$) [11], and $b = 0.76$ for silica at $1530^\circ C$ (experimental $b = 0.70$).^{*} Although such agreement is presumably only fortuitous, it may nonetheless prove useful.

DISCUSSION

The one assumption of this approach is that the activation energy (or activation barrier) of the relaxation process is time dependent. Hence, the activation energy is considered to be

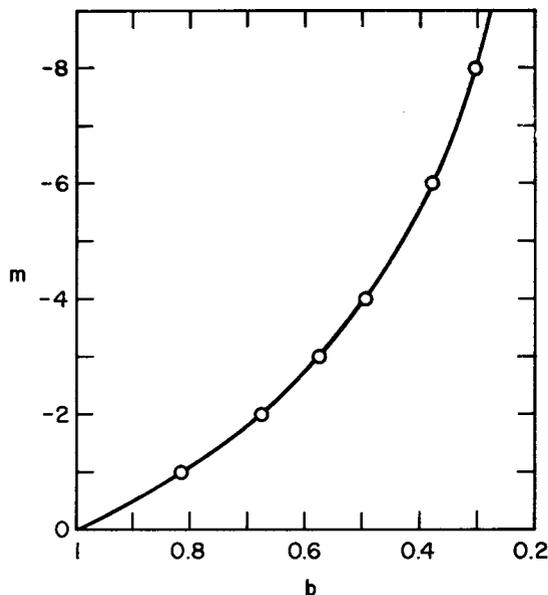


Fig. 5 — Correspondence between values of parameters of b and m . The line represents the empirical equation $1/b = 1 - 0.227m + 0.0076m^2$.

^{*}J. A. Bucaro, private communication.

a dynamic property, in much the same manner as compressibility, thermal expansivity, and heat capacity are conventionally considered. Such an approach is plausible only if the activation energy is not required to change by a large amount during the course of the relaxation. For the glasses tested (including B_2O_3 , silica, and soda-lime glasses), the total required change is only 3.6% ($a_m = 0.0355$). It is therefore not unreasonable to suggest the presence of such a small dynamic effect.

This time-dependent activation energy can be interpreted as arising from a physical origin: all structural units are initially equivalent, but as the first units relax, they form configurations or energy states that tend to stabilize the other as yet unrelaxed units in their immediate environment. The remaining unrelaxed structural units then experience an activation barrier that is somewhat larger than that encountered by the first units to relax.

This physical interpretation is particularly consistent with the use of $M(t)$ as the reaction coordinate. With this choice, the extent to which an unrelaxed unit is stabilized becomes simply proportional to the number of relaxed units present in its immediate environment. It must be noted, however, that to avoid memory complications [12], $M(t)$ should not be viewed as a state parameter.

A further feature of glassy relaxations is their tendency to be highly nonlinear. Narayanaswamy has suggested that finite-perturbation (nonlinear) behavior can be included as an ad hoc activation energy correction [3]. Thus a typical data reduction procedure is to use the fractional exponential equation for the linear behavioral component [13], and an expression of entirely different form (Narayanaswamy's) to account for deviations from linearity.

By using the formulation presented in this report for the linear component, the linear and nonlinear equations merge. Narayanaswamy's correction now appears as simply an additional fictive, temperature-dependent term in Eq. (8). The resulting unification of linear and nonlinear equations is not only a computational aid, but also makes possible the future inclusion of cross terms (e.g., dependence of width on the magnitude of the perturbation).

Finally, it has been often noted that glassy relaxation processes generally differ from simple relaxation theory in three respects: their widths are broader, their activation energies are temperature dependent, and they are highly nonlinear. It is interesting that all three factors can be attributed to the variability of just one relaxation property—activation energy.

CONCLUSIONS

The assumption was made that activation energy can be time dependent. Some phenomenological consequences of this assumption were investigated. The formulation developed is found to be phenomenologically more descriptive of experimental data than any previous formulation. However, it is recognized that the body of data available for such tests (for example, the temperature dependence of b or the functional form of the nonlinearity correction) is rather limited. Hence, of necessity, this report is somewhat speculative.

The principal conclusion of this study is that the approach presented is demonstrably useful and offers considerable potential for further development.

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Appendix A

DERIVATION FOR THE CASE $x(t) = \ln t/\lambda$

With $\ln t/\lambda$ as a choice of reaction variable $x(t)$, Eqs. (8) and (12) yield

$$\lambda(t) = A_f \exp \left[\frac{E_a^\circ}{RT} \left(1 + a_f \ln \frac{t}{\lambda^\circ} \right) \right] \quad (\text{A1})$$

Where the subscript f is used to indicate parameters whose value is specific to this choice of reaction variable. Equation (A1) readily reduces to

$$\lambda(t) = \frac{A_f \lambda^\circ}{A^\circ} \left(\frac{t}{\lambda^\circ} \right)^{1-b} \quad (\text{A2})$$

where b is defined as

$$b \equiv 1 - \frac{a_f E_a^\circ}{RT} \quad (\text{14})$$

and where $A^\circ \equiv \lambda^\circ \exp(E_a^\circ/RT)$, which is a constant to be eliminated shortly.

Substituting Eq. (14) into Eq. (7) and integrating yield

$$M(t) = \exp \left[-\frac{A^\circ}{b A_f} \left(\frac{t}{\lambda^\circ} \right)^b \right]. \quad (\text{A3})$$

With use of the constraint, Eq. (5), this expression reduces to the simple form,

$$M(t) = \exp \left[-\left(\frac{t}{\lambda^\circ} \right)^b \right]. \quad (\text{13})$$

Appendix B

DERIVATION FOR THE CASE $x(t) = M(t)$

With the selection of $M(t)$ for the reaction variable $x(t)$, Eqs. (8) and (12) become

$$\lambda(t) = A^\circ \exp \left[\frac{E_a^\circ}{RT} \frac{1 + a_m M(t)}{1 + a_m/e} \right] \quad (\text{B1})$$

or

$$\lambda(t) = A' \exp [mM(t)], \quad (\text{B2})$$

where A' is a constant, which will be eliminated shortly, and m is defined as

$$m \equiv \frac{a_m}{1 + a_m/e} \frac{E_a^\circ}{RT} \quad (\text{16})$$

Here a_m is parameter a in Eq. (1) whose value is specific to this choice of reaction variable. Note that the values of a_m and m are both negative, since $M(t)$ decreases as the relaxation proceeds.

Combining Eqs. (7) and (B2) and integrating yield

$$\frac{t}{A'} = Ei(m) - Ei(mM(t)) \quad (\text{B3})$$

where Ei is the exponential integral,* which can be evaluated from tables, or from the infinite series expansion:

$$Ei(x) = 0.57722 + \ln x + \sum_{n=1}^{\infty} \frac{x^n}{n(n!)} \quad (\text{B4})$$

Evaluating Eq. (18) at $t = \lambda^\circ$ to eliminate A' yields the final expression:

$$\frac{t}{\lambda^\circ} = \frac{Ei(m) - Ei(mM(t))}{Ei(m) - Ei(m/e)} \quad (\text{15})$$

*E. Jahnke, F. Emde, and F. Lösch, *Tables of Higher Functions*, 6th ed. (revised by F. Lösch), McGraw-Hill, New York, 1960, p. 17.

1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. This is essential for ensuring transparency and accountability in the organization's operations.

2. The second part of the document outlines the various methods and techniques used to collect and analyze data. This includes both qualitative and quantitative approaches, as well as the use of advanced statistical tools and software.

3. The third part of the document focuses on the interpretation and application of the collected data. This involves identifying key trends, patterns, and insights that can inform decision-making and strategic planning.

4. The fourth part of the document discusses the challenges and limitations of data analysis. This includes issues such as data quality, bias, and the potential for misinterpretation, as well as the need for ongoing monitoring and evaluation.

5. The fifth part of the document provides a summary of the key findings and conclusions. This highlights the overall impact of the data analysis and offers recommendations for future research and practice.

6. The sixth part of the document includes a list of references and sources used in the research. This provides a clear and concise overview of the literature and resources that informed the study.

7. The seventh part of the document contains a list of appendices and supplementary materials. This includes additional data, charts, and tables that provide further detail and support for the main findings.

8. The eighth part of the document includes a list of acknowledgments and a list of authors. This recognizes the contributions of all individuals and organizations that supported the research and its publication.

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