Acceleration Transforms and Statistical Kinetic Models

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For a restricted class of problems a mathematical model of microscopic degradation processes, statistical kinetics, is developed and linked through *acceleration transforms* to the information which can be obtained from a system in which the only observable sign of degradation is sudden and catastrophic failure. The acceleration transforms were developed in accelerated life testing applications as a tool for extrapolating from the observable results of an accelerated life test to the dynamics of the underlying degradation processes. A particular concern of a physicist attempting to interpreted the results of an analysis based on acceleration transforms is determining the physical species involved in the degradation process. These species may be (a) relatively abundant or (b) relatively rare. The main results of this paper are a theorem showing that for an important subclass of statistical kinetic models, acceleration transforms cannot be used to distinguish between cases a and b, and an example showing that in some cases falling outside the restrictions of the theorem, cases a and b can be distinguished by their acceleration transforms.

1. INTRODUCTION

The models proposed and discussed in this paper apply to phenomena more familiar to an industrial or a biological setting than to a physics laboratory. The phenomenon of concern is the degradation of complex material systems such as printed wiring boards, integrated circuits, rats, or ecosystems. The purpose of this paper is to discuss a class of mathematical models that can be used to model observables associated with the degradation of such systems. The focus of this paper will be on building

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models of the relatively microscopic phenomena leading to failures in a system, when all that can be observed are the stresses the system is subject to and the times when individual systems (units) suddenly and catastrophically collapse. The models of the "relatively" microscopic processes we call statistical kinetic models, and the models we derive from them to describe the observable data are called acceleration transforms.[1] The reason for constructing two tiers of models, leading from microscopic phenomena to observable data and back, is that the models constructed from the observable degradation phenomena are used to extrapolate to conditions where no data have been taken. In order to minimize the Malthusian nature of such extrapolations, our philosophy is to always try to deduce a theory of the degradation phenomena being considered rather than just fit a curve to observed degradation data. Such a theory requires that the measurable phenomena provide information about the microscopic processes causing the degradation. Acceleration transforms provide us with a tool to deduce the necessary microscopic information from the macroscopic measurements.

Acceleration transforms are models of failure time data which meet two criteria:

1. The models reflect the processes giving rise to failure.
2. The models reflect the fact that the initial conditions vary between individual units and are unknown because of the expense it would take to gather the information.

Originally[1] these models were developed assuming that all relevant degradation processes could be described by systems of deterministic differential equations. The randomness of the models was due entirely to the variations in initial conditions between experimental units. Using simulated data, it was found that data analysis methods based on acceleration transforms could be used to differentiate among processes dominated by a single step, competing processes, and sequential processes. However, when we applied the model to experimental data generated in accelerated life tests, it became apparent that interpreting our models deterministically might be inappropriate, and that it was important to understand what the effect on the models would be if we assumed that the processes were very slow, governed by stochastic transition of a small number, say 10^2–10^9, of molecules or perhaps objects larger than molecules. We consider this the domain of statistical kinetics.

A very restricted form of a statistical kinetic model is developed in Section 2, and four examples of processes are given. In Section 3 it is argued that for a restricted class of statistical kinetic models the derived acceleration transforms are identical to acceleration transforms derived

from corresponding deterministic models. Section 3 concludes by describing the acceleration transforms for the four previously developed examples of statistical kinetic processes. In particular, the fourth example demonstrates that the identity described above does not hold in general. The final section contains a discussion of scientific and data analytic problems, some solved and some unsolved, associated with the application of the framework provided by acceleration transforms and statistical kinetic models to the analysis of industrial accelerated life test data.

2. STATISTICAL KINETIC MODELS

Our model of degradation is based on the assumption that in any physical system, degradation can be described as a two-step process: (1) Microscopic flaws are generated through random accidents; (2) Subsequent changes in the state of the collection of microscopic flaws result in changes in the macroscopic behavior of the system.

For the purpose of this paper statistical kinetics is concerned with the second step, assuming a particular distribution of flaws to start with. For example, we may begin with a crystal containing a collection of impurities and dislocations. The dislocations move freely until they are trapped. As more dislocations accumulate, a microcrack is formed, which quickly extends to a crack. As another example, consider the region between two oppositely biased, copper-plated through-holes in an epoxy glass printed wiring board. The flaws in this case may be molecules of halogenic acids left over from manufacturing processes. With sufficient humidity the halogenic ions may participate in chemical reactions, which cause the formation of conductive filaments reaching from the anode to the cathode.[1]

Given the two examples, we see that even though we are leaving out step 1, the formulation described in this paper still has to cover a broad range of phenomena. The first example requires not only that the state of the flaws be tracked, but also that the distribution of energy throughout the crystal be tracked. The second example requires the generality to describe both chemical and electrochemical reactions.

Actually, our goal in this paper is much more modest than a full elucidation of statistical kinetics. The mathematics developed in this paper is meant to deal with a collection of physical systems, indexed by $\omega \in \Omega$, where the systems degrade in the same manner and where each system satisfies the following postulates:

P1. At time t, system ω may be completely described (with respect to variables affecting the degradation process) by the pair $(D_\omega(t), s(t))$, where the vector $D_\omega(t)$ is the vector describing the state of each flaw in the system

and $s(t)$ is the stress (e.g., energy fields, material environment, etc.) to which the system is subject at time t. The restrictive part of this assumption is that we are assuming that except for the flaws, the physical system we are discussing immediately equilibrates with its surrounding environment.

P2.   The degradation process is described by a set of states A_i and transition intensities k_{ij} such that given $D_\omega(t)$ and $s(t)$, for each pair of states (A_i, A_j) there exist a nonnegative constant $k_{ij}(D_\omega(t), s(t))$ such that for any flaw δ in state A_i

$$\lim_{\Delta \to 0} \left[\frac{P(\delta \in A_j : t + \Delta \mid \delta \in A_i : t)}{\Delta} \right] = k_{ij}(D_\omega(t), s(t)) \tag{1}$$

Here $P(\delta \in A_j : t + \Delta \mid \delta \in A_i : t)$ is read "the probability that flaw δ is in state A_j at time $t + \Delta$ conditionally given that δ is in state A_i at time t." The dependence of k_{ij}, the transition intensity between state i and state j, in Eq. (1) on $D_\omega(t)$ and $s(t)$ implicitly allows for phenomena such as occur in the crystal example, where the change in state of any flaw changes the stress field in the crystal, thus changing the probability of transitions by other flaws. For notational convenience we will stop denoting the dependence of k_{ij} on $s(t)$ for the rest of this section.

P3.   The function $s(t)$ is nonrandom and $D_\omega(t)$ is Markov, given the function $s(t)$.

P4.   The directed graph describing the allowable transitions for individual flaws has no cycles, and hence transitions are irreversible. This postulate can be defended on physical grounds as a good approximation for many, but not all, degradation processes. In many cases degradation is either being driven by external energy sources or is associated with a macroscopic increase in entropy (e.g., diffusion-driven processes). By defining the set of states that flaws can occupy grossly enough, the processes will be essentially irreversible. For example, a dislocation may be defined either as free or tangled, rather then being defined more finely by its position. This gross definition of states can lead one to question the accuracy of Postulate P2. We will use P2 because we assume that it provides a reasonable approximation to the truth, and it is relatively easy to handle.

Note that P4 implies that if there is only a finite number of states, at least one must be an *absorbing* state, a state from which no other state is accessible. We specify that one of these absorbing states is special, in that it causes failure. We denote this special state by M, and, anticipating the development in the next section, we say that for each experimental unit ω there exists a threshold $\langle M \rangle_\omega$ so that when the number or flaws in state M reaches $\langle M \rangle_\omega$, the unit fails.

In our discussion of statistical kinetics, it is more convenient to use a form of stochastic differential equation than to use equations of the form given by Eq. (1). To see in a simple case how this form may be derived from (1), suppose that $i = 1$, $j = 2$, and that A_1 and A_2 are the only states in which flaws may occur. By the definition of conditional probability, (1) can be written as

$$\lim_{\Delta \to 0} \left[\frac{P(\delta \in A_2 : t + \Delta) - P(\delta \in A_2 : t)}{\Delta} \right] = k_{12}(D_\omega(t)) \, P(\delta \in A_1 : t)$$

or more succinctly

$$(d/dt) \, P(\delta \in A_2 : t) = k_{12}(D_\omega(t)) \, P(\delta \in A_1 : t) \tag{2}$$

In interpreting the above, recall that each probability statement is conditioned on $D_\omega(t)$. If we use $\langle A_j \rangle(t)$ to denote the expected number, again conditioned on $D_\omega(t)$, at time t (or some fixed scalar multiple of a number such as concentration) of flaws in state A_j at time t, (2) is equivalent to

$$(d/dt)\langle A_1 \rangle(t) = k_{12}(D_\omega(t))\langle A_2 \rangle(t) \tag{3}$$

Those familiar with chemistry will note that Eq. (3) looks like a differential equation drawn from a system describing a first-order chemical reaction. This is no accident, since the deviation given above is a simplification of the derivation used to develop the so-called "master equation" (see ref. 3 and references therein), which can be used to tie together the stochastic behavior of individual molecules and chemical kinetics.

Before proceeding to some particular examples to show how particular models of the form given in (3) may be applied, we discuss some results concerning the structure of a simplified class of models.

We define a statistical kinetic model to be *simple* if all of the transition intensities are functionally independent of $D_\omega(t)$. The mathematics we derive from this point on is derived by conditioning only on $D_\omega(0)$ unless specifically stated otherwise (i.e., example 4). This actually is quite reasonable for the class of simple statistical kinetic models, since the expected probabilities are equal to the limiting frequencies in that class. The importance of this point has to do with the fact that the acceleration transforms associated with these models are identical whether the unit-to-unit variability is due *only* to differences in initial conditions or due to both a difference in initial conditions and stochastic transitions (see Theorem 1). This identity is not necessarily true for other statistical kinetic models. An example of a model for which this is not true is given as example 4.

The following facts may be derived from postulates P1–P4 and our

definition of simple statistical kinetic models. These facts will be useful in proving later results.

Fact 1. Begin by noting that P4 and the definition of simple statistical kinetic models implies that the finite set of states $A_1,..., A_m$ can be relabeled so that $A_m = M$, and that given any i, only states A_j with $j < i$ can access A_i. The proof that this reordering can be accomplished follows easily by induction. That the result is true for three states follows by exhausting all cases. Assume that the reordering can be done for any $(m-1)$-state system satisfying the postulates and consider an m-state system. By P4 and the fact that the system is finite, there exists a state, which we will call A_0, such that A_0 is not accessible from any other state. By the induction hypothesis, the other $(m-1)$ states may be relabeled as $A_1,..., A_{(m-1)}$, so that they satisfy the condition of the first sentences. Relabeling A_i as A_{i+1} proves that the reordering can always be accomplished. It is then possible (through this relabeling of states) to write the system of differential equations corresponding to a simple statistical kinetic model with states $A_1,..., A_m$ as a triangular system of differential equations of the form

$$(d/dt)\langle A_i \rangle(t) = k_{1i}\langle A_1 \rangle(t) + \cdots + k_{i-1,i}\langle A_{i-1} \rangle(t) - k_{ii}\langle A_i \rangle(t)$$

To see this, note that by summing equations of form (1) over all states accessing A_i and summing the appropriate modification of (1) over all states accessible from A_i and then applying the definition of conditional probability, we see that

$$\lim_{\Delta \to 0} \left[\frac{P(\delta \in A_i: t+\Delta) - P(\delta \in A_i: t)}{\Delta} \right]$$

$$= \sum_{j<i} k_{ji} P(\delta \in A_j: t) - \left(\sum_{j>i} k_{ij} \right) P(\delta \in A_i: t)$$

Defining $k_{ii} = \sum_{j>i} k_{ij}$, taking the limit, and summing over the set of all flaws in unit ω gives the result.

Until this point, we have not denoted the dependence of all of these probabilities or expected numbers of units on the particular realization of the material system. As we proceed this will become more important, so we add the following conventions to our notation. We will use $B: t, \omega$ to denote that the event B holds at time t in unit ω, and we use $\langle A \rangle_\omega(t)$ and $\{A\}_\omega(t)$ to denote, respectively, the expected number of flaws in state A at time t in unit ω and the actual number of flaws in state A at time t.

The next elementary fact allows us to derive a partial description of the distribution of time to failure.

Fact 2. For simple statistical kinetic models, if no two nonzero k_{ii} are identical, the solution to the system of differential equations takes the form

$$\langle A_i \rangle_\omega(t) = \sum_{j=1}^{i} a_{ji\omega} \exp(-k_{jj}t) \tag{4}$$

$$\langle M \rangle_\omega(t) = \sum_{i=1}^{m-1} \left[\langle A_i \rangle_\omega(0) - \sum_{j=1}^{i} a_{ji\omega} \exp(-k_{jj}) \right]$$

where we assume $\langle M \rangle_\omega(0) = 0$, and where the a_{ji} are rational functions of the $\langle A_i \rangle_\omega(0)$ and the k_{ij}. This fact follows immediately from Fact 1 and our definitions.

Define n_ω as the number of flaws that may potentially reach state M. From Fact 2, the independence of the flaws implied by the Markov property of the system, and the fact that the k_{ij} are independent of $D_\omega(t)$, we see that the probability that any randomly selected flaw δ is in state M at time t in unit ω is

$$P(\delta \in M \colon t, \omega) = \frac{\langle M \rangle_\omega(t)}{n_\omega}$$

$$= \left\{ \sum_{i=1}^{m-1} \left[\langle A_i \rangle_\omega(0) - \sum_{j=1}^{i} a_{ji\omega} \exp(-k_{jj}t) \right] \right\} n_\omega^{-1} \tag{5}$$

By the independence noted above, and recalling the definition of $\langle M \rangle_\omega$, we see that the probability of failure in unit ω by time t may be written

$$\sum_{i=\langle M \rangle_\omega}^{n_\omega} \binom{n_\omega}{i} P(\delta \in M \colon t, \omega)^i [1 - P(\delta \in M \colon t, \omega)]^{n_\omega - i} \tag{6}$$

From (5) and (6) we see that the observable failure distribution is a function of the system of differential equations particular to the simple statistical kinetic model (which we denote by E) and the distribution over Ω (the population of ω's) of the triple $(n_\omega, \langle M \rangle_\omega, D_\omega(0))$.

To examine the implications of the development thus far, and to set the stage for the introduction of acceleration transforms, we will now examine four examples of statistical kinetic models. Three of these models will be simple statistical kinetic models. The fourth is the simplest member of a more general class of statistical kinetic models.

Example 2.1. The Single-Step Process

For additional clarity, we adopt the arrow notation used in chemical kinetics. Thus

$$A \xrightarrow{k_1} M \tag{7}$$

may be read as flaws move from state A to state M with transition intensity k_1. The arrow diagram (7) is the one representing the single-step process. The corresponding system of differential equations is

$$(d/dt)\langle A \rangle_\omega(t) = -k_1\langle A \rangle_\omega(t)$$
$$(d/dt)\langle M \rangle_\omega(t) = k_1\langle A \rangle_\omega(t) \tag{8}$$

In our general notation $A = A_1$, $M = A_2$, and $k_{11} = k_{12} = k_1$. The solution to (8) has the form

$$\langle M \rangle_\omega(t) = \langle A \rangle_\omega(0)[1 - \exp(-k_1 t)] \tag{9}$$

Since $\langle A \rangle_\omega(0) = n_\omega$ in this model, we find

$$P(\delta \in M: t, \ \omega) = 1 - \exp(-k_1 t) \tag{10}$$

Possible examples of degradation processes following this model include degradation processes limited by a pseudo-first-order chemical reaction[2] and processes limited by the effect of a homogeneous Poisson process, such as destruction of memory cells on an integrated circuit through the impact of high-energy cosmic rays. The latter is an example where step 1 of our model of degradation dominates rather than step 2.

    In this very simple example, it is interesting to note the tradeoffs that can occur between randomness induced by the degradation process and randomness induced by the initial conditions. With a pseudo-first-order chemical reaction, assuming the reaction involves more than 10^{20} flaws (molecules), randomness in the observed failure distribution is due entirely to differences in initial conditions. On the other hand, in a computer memory with no redundancy a single cell failure can ruin the system, so the randomness in this case comes entirely from the transition process.

Example 2.2. A Simple Sequential Process

    This model is applicable when the process has two steps occurring in sequence which dominate the rate of the process over the observable range of applied stress. For example, in a constant-relative-humidity environment, the release of small amounts of corrosive impurities from a polymer matrix followed by the attack of those impurities on a copper conductor would be such a process. As long as the reactions are pseudo-first order this model should fit. Another possible model is that of a very delicate site requiring two "hits" by two types of molecules in sequence to cause failure. If the concentration is low in the environment of the site, the hits should follow independent Poisson distributions, leading to this sequential model. Cancer initiation and promotion might be modeled this way.

The arrow diagram for this model is

$$A \xrightarrow{\;k_1\;} B \xrightarrow{\;k_2\;} M \tag{11}$$

The system of differential equations corresponding to (11) is

$$(d/dt)\langle A \rangle_\omega(t) = -k_1 \langle A \rangle_\omega(t)$$

$$(d/dt)\langle B \rangle_\omega(t) = k_1 \langle A \rangle_\omega(t) - k_2 \langle B \rangle_\omega(t) \tag{12}$$

$$(d/dt)\langle M \rangle_\omega(t) = k_2 \langle B \rangle_\omega(t)$$

In the general notation $A = A_1$, $B = A_2$, $M = A_3$, $k_1 = k_{11} = k_{12}$, $k_2 = k_{22} = k_{23}$, and $k_{13} = 0$. The solution of (12) for $\langle M \rangle_\omega(t)$ is

$$\langle M \rangle_\omega(t) = \langle A \rangle_\omega(0)\left[1 + \frac{k_1}{k_2 - k_1}\exp(-k_2 t) - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) \right]$$

$$+ \langle B \rangle_\omega(0)[1 - \exp(-k_2 t)] \tag{13}$$

Thus,

$$P(\delta \in M: t, \omega) = P_\omega\left[1 + \frac{k_1}{k_2 - k_1}\exp(-k_2 t) - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) \right]$$

$$+ (1 - P_\omega)[1 - \exp(-k_2 t)] \tag{14}$$

where

$$P_\omega = \frac{\langle A \rangle_\omega(0)}{\langle A \rangle_\omega(0) + \langle B \rangle_\omega(0)}$$

Latent defects present in a subpopulation could be incorporated into a model of this sort by assuming $P_\omega = 1$ for all units in the population except defective units.

Example 2.3. A Competing Processes Model

In this model the degradation process is assumed to be dominated by two single-step processes competing for the same resource. One of these processes leads to state M, and the other to a state from which M is inaccessible. For example, if the rate-limiting step in a process causing degradation in an electrical insulator is polymer degradation resulting from impurities in the polymer matrix, while a side reaction is consuming some of these impurities, and if the reactions are all pseudo-first-order reactions, then this mathematical model would be appropriate. Another situation in

which this model might be appropriate involves the population dynamics of microbe cultures, in which the failure-causing process would be periodic flushing of the region in which the culture is growing with toxic chemicals, and the competing process is mutation causing changes in microbes that make them able to survive such flushing. In this case the experimental units would be populations of microbes within a location.

The arrow diagram for this process is:

$$
A \underset{k_2}{\overset{k_1}{<}} \begin{matrix} M \\ \\ B \end{matrix} \tag{15}
$$

The system of differential equations corresponding to (15) is

$$
(d/dt)\langle A \rangle_\omega(t) = -(k_1 + k_2)\langle A \rangle_\omega(t)
$$

$$
(d/dt)\langle B \rangle_\omega(t) = k_2 \langle A \rangle_\omega(t) \tag{16}
$$

$$
(d/dt)\langle M \rangle_\omega(t) = k_1 \langle A \rangle_\omega(t)
$$

In the general notation, $A = A_1$, $B = A_2$, $M = A_3$, $k_{11} = k_1 + k_2$, $k_{12} = k_2$, $k_{13} = k_1$, $k_{23} = k_{22} = 0$. The solution for $\langle M \rangle_\omega(t)$ is

$$
\langle M \rangle_\omega(t) = \langle A \rangle_\omega(0) \left(\frac{k_1}{k_1 + k_2} \right) \{ 1 - \exp[-(k_1 + k_2)t] \} \tag{17}
$$

Thus,

$$
P(\delta \in M: t, \omega) = \frac{k_1}{k_1 + k_2} \{ 1 - \exp[-(k_1 + k_2)t] \} \tag{18}
$$

Remark 1. The right-hand sides of both (18) and (10) are functionally independent of the experimental unit ω. This property will turn out to be useful when defining acceleration transforms. Unfortunately, (14), that is, $P(\delta \in M: t, \omega)$ for the sequential model cannot be expressed in this manner unless it is assumed that P_ω is constant across the ω. This makes the expression and solution of the transform derived from (14) far more difficult than those derived from (10) or (18).

The final example is one of the nonsimple models. We will call these models stochastically coupled because the transition behaviors of the flaws are coupled together stochastically.

Example 2.4. A Stochastically Coupled Model

The arrow diagram for this model can be written

$$A \xrightarrow{\;k_1\;} B \tag{19}$$

$$C \xrightarrow{\;k_2\{B\}_\omega(t)\;} M$$
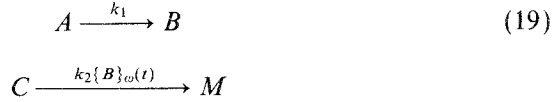
The accompanying system of differential equations is

$$(d/dt)\langle A \rangle_\omega(t) = -k_1 \langle A \rangle_\omega(t)$$
$$(d/dt)\langle B \rangle_\omega(t) = k_1 \langle A \rangle_\omega(t)$$
$$(d/dt)\langle C \rangle_\omega^B(t) = -k_2\{B\}_\omega(t)\langle C \rangle_\omega^B(t) \tag{20}$$
$$(d/dt)\langle M \rangle_\omega^B(t) = k_2\{B\}_\omega(t)\langle C \rangle_\omega^B(t)$$

where $\langle C \rangle_\omega^B(t)$ is the expected number of flaws in C at time t in unit ω, conditionally given $D_\omega(t)$ at time 0 in unit ω and the history of $\{B\}_\omega$. In terms of the general notation $A = A_1$, $B = A_2$, $C = A_3$, $M = A_4$, $k_{11}(D_\omega(t)) = k_{12}(D_\omega(t)) = k_1$, $k_{13}(D_\omega(t)) = k_{23}(D_\omega(t)) = k_{14}(D_\omega(t)) = k_{24}(D_\omega(t)) = 0$, and $k_{34}(D_\omega(t)) = k_2\{B\}_\omega(t)$.

This particular model might be appropriate in modeling failure caused by corrosion, when the corrosion rate is dependent on the generation of an ionic species in a separate hydrolysis reaction. We will assume for convenience that $\langle B \rangle_\omega(0) = 0$. The formal solutions to (20) in $\langle B \rangle_\omega(t)$ and $\langle M \rangle_\omega^B(t)$ are

$$\langle B \rangle_\omega(t) = \langle A \rangle_\omega(0)[1 - \exp(-k_1 t)] \tag{21}$$

$$\langle M \rangle_\omega^B(t) = \langle C \rangle_\omega(0) \left\{ 1 - \exp\left[-k_2 \int_0^t \{B\}_\omega(s)\, ds \right] \right\} \tag{22}$$

Defining

$$\beta_\omega(t) = [\{B\}_\omega(t) - \langle B \rangle_\omega(t)]/\langle A \rangle_\omega(0)$$

one may expand Eq. (22):

$$\langle M \rangle_\omega^B(t) = \langle C \rangle_\omega(0) \left(1 - \exp\left\{ -k_2 \langle A \rangle_\omega(0) \left[\left(t - \frac{1 - \exp(-k_1 t)}{k_1} \right) \right. \right. \right.$$
$$\left. \left. \left. + \int_0^t \beta_\omega(s)\, ds \right] \right\} \right) \tag{23}$$

Define $\beta^*{}_\omega[1 - \exp(-k_1 t)] = \beta_\omega(t)$. Then $\beta^*{}_\omega(t)$, $0 < t < 1$, is the centered empirical distribution function of a sample of size $\langle A \rangle_\omega(0)$ drawn from a uniform distribution on $(0, 1)$. Thus the term $\langle A \rangle_\omega(0)^{1/2}\beta^*{}_\omega(t)$, $0 < t < 1$, can be approximated by a standard Brownian bridge.[4] Taking the expected value of (23) conditionally given ω (expectation is with respect to the conditional probability distribution placed on the flaws) gives the approximation

$$\langle M \rangle_\omega(t) = \langle C \rangle_\omega(0) \left\{ 1 - \exp\left[-k_2\langle A \rangle_\omega(0) \left(t - \frac{1 - \exp(-k_1 t)}{k_1} \right) \right] \right.$$

$$\left. \times \exp\left(\frac{-k_2^2}{2k_1^2} \langle A \rangle_\omega(0) \, \sigma^2(t) \right) \right\} \tag{24}$$

where $\sigma^2(t)$ is

$$2[1 - \exp(-k_1 t) - k_1 t \exp(-k_1 t)] - [1 - \exp(-k_1 t)]^2 \tag{25}$$

which is just the variance of the random variable formed by integrating the standard Brownian bridge with respect to the weight function $1/(1 - s)$, the Jacobian for the change of variable, from 0 to $1 - \exp(-k_1 t)$.

A simple derivation of (25), which was provided to the authors by V. J. Nair and C. L. Mallows simultaneouly during a discussion, is as follows. If $\beta(s)$ is a Brownian bridge on the interval 0, 1, then

$$\sigma^2(t) = E\left[\int_0^u \int_0^u \frac{\beta(s)\,\beta(t)}{(1 - s)(1 - t)} \, ds \, dt \right]$$

By exchanging expectation and integration this becomes

$$\int_0^u \int_0^u \frac{\min(s, t) - st}{(1 - s)(1 - t)} \, ds \, dt = 2[u + \log(1 - u) - u \log(1 - u)] - u^2$$

substituting $1 - \exp(-k_1 t)$ for u gives the result.

If we wish to calculate the probability of failure in unit ω by time t given only the initial conditions, we may still use (6), because conditionally given the sample path of $\{B\}_\omega$, the sample paths of the flaws that can end in M are independently and identically distributed.

Remark 2. In order for the process (19) to take noticeable time and to be noticeably different from (7), it is necessary that the terms

$$k_2\langle A \rangle_\omega(0) \left(t - \frac{1 - \exp(-k_1 t)}{k_1} \right) \quad \text{and} \quad \frac{1}{\exp(-k_1 t)}$$

be bounded for t in the range of observable time. Thus, as $\langle A \rangle_\omega(0)$ increases, $k_2\{t - [1 - \exp(-k_1 t)]/k_1\}$ must decrease. The first expression above for small $k_1 t$ has a Taylor expansion $k_2 k_1 t^2$. Since t is bounded by the sensitivity of the procedure we are using for measurement, we see that $k_2 k_1$ must be proportional to $\langle A \rangle_\omega^{-1}(0)$ [for simplicity $\langle A \rangle_\omega(0)$ will be denoted as n for the rest of this argument].

Now, suppose $k_2 \propto n^{-p}$ and $k_1 \propto n^{-(1-p)}$. Then the exponent in the third exponential term in expression (24) is proportional to $n^{2[(1-p)-p]} * n * \sigma^2(t)$. But by Taylor expansion, for small $k_1 t$, $\sigma^2(t) \propto k_1^3$. Thus, the term in question is

$$n^{2[(1-p)-p]} * n * n^{-3(1-p)} = n^{-p}$$

For values of $p \leqslant 0$, the third exponent remains, because k_1 is small enough relative to $\langle A \rangle_\omega(0)$ so that the effect of the change from state A to state B is noticeably stochastic. However, for $p > 0$, as $\langle A \rangle_\omega(0)$ gets large, $\langle M \rangle_\omega(t)/\langle C \rangle_\omega(0)$ or $P(\delta \in M: t \mid \delta \in C: 0)$, which corresponds to $P(\delta \in M: t)$ in the simple statistical kinetic models, converges to

$$1 - \exp\left[-k_2 \langle A \rangle_\omega(0) \left(t - \frac{1 - \exp(-k_1 t)}{k_1} \right) \right] \qquad (26)$$

In the next section it will be shown that this change in the form of $P(\delta \in M: t \mid \delta \in C: 0)$ with change in the size of $\langle A \rangle_\omega(0)$ actually causes a change in the amount of information that the macroscopic observable, via acceleration transforms, contains about the underlying process. Such a property does not hold with simple statistical kinetic models.

3. ACCELERATION TRANSFORMS

Acceleration transforms are built upon statistical kinetic models of degradation processes. Recall from the discussion following expressions (5) and (6) that the distribution of failure times at any given stress condition is a function not only of the system of equations, but also of the distribution of the unit specific parameters. Acceleration transforms allow us to separate the effects of the system of equations from the effects of unit-to-unit variation. This separation allows the development of data analytic estimation and model selection procedures that can be used directly to provide insights into the degradation process.

The rest of this section will follow the same program as that used in the latter part of Section 2. First we derive a theoretical result concerning the structure of acceleration transforms constructed from simple statistical

kinetic models under some regularity conditions. Then we examine acceleration transforms derived from the simple statistical kinetic models developed in Section 2. Finally, we present and discuss two acceleration transforms derived from our stochastically coupled example.

A key technical point in understanding the difference between this section and the last section is that calculations in the last section were performed conditionally given a single experimental unit ω. Calculations in this section are based on averaging over the population Ω of experimental units.

The theorem is proven under the following assumptions:

Assumption 1. Except for the transition intensities, which vary with applied stress, the degradation process occurring at all stress conditions can be described using the same simple statistical kinetic model.

Assumption 2. $\langle M \rangle_\omega$, the number of flaws in state M necessary to trigger failure in unit ω, is independent of stress, as is n_ω.

Assumption 3. The ratios $\langle A_i \rangle_\omega(0)/n_\omega$ are all constant across Ω and stress conditions.

This last assumption is extremely restrictive, and we feel that it is probably unnecessary.

To state the theorem, we need to define the concept of equivalent time. A time t_1 under stress condition s_1 corresponds to an equivalent time t_2 under stress condition s_2 only if the probability of failure before time t_1 under s_1 is the same as the probability of failure before the time t_2 under s_2. We assume throughout this section that applied stress does not vary with time.

Theorem. Under the above assumptions and those of Fact 2, the transformation taking time under one stress condition s_1 to the equivalent time at another stress condition s_2, when such equivalent time exist (e.g., see the third example in this section), can be expressed as a function involving only the system of equations E, the transition intensities at each condition, and the ratios $P_i = \langle A_i \rangle_\omega(0)/n_\omega$.

Proof. Formulas (5) and (6) describe the probability of failure in unit ω by time t. Fact 2 and assumption 3 together imply that $P(\delta \in M: t, \omega)$ is functionally independent of the experimental unit ω. Thus, the probability of failure by time t in the population Ω can be written

$$\int_\Omega \left\{ \sum_{i=\langle M \rangle_\omega}^{n_\omega} \binom{n_\omega}{i} P(\delta \in M: t)^i [1 - P(\delta \in M: t)]^{n(\omega)-i} \right\} dF(\omega)$$

where $F(\omega)$ is the bivariate probability distribution function of the pair $(\langle M \rangle_\omega, n_\omega)$ over Ω. Assumption 2 implies that $F(\omega)$ will not change as stress changes, so the change in the failure distribution between s_1 and s_2 is a monotone function of the change in the term $P(\delta \in M: t, s_1)$ $[P(A: t, s)$ is the probability that event A occurs at time t under stress condition $s]$. Thus the transformation taking t_1 to t_2 satisfying $P(\delta \in M: t_2, s_2)$ in the same transformation taking the time elapsed under stress condition s_1 to the equivalent time elapsed under stress condition s_2.

From Fact 2 and assumption 3 we can see that this transformation is simply the implicit function taking t_1 to t_2 defined by the equation

$$\sum_{i=1}^{m} \left\{ P_i - \sum_{j=1}^{i} b_{ji}(s_1) \exp[-k_{jj}(s_1)t_1] \right\}$$

$$= \sum_{i=1}^{m} \left\{ P_i - \sum_{j=1}^{i} b_{ji}(s_2) \exp[-k_{jj}(s_2)t_2] \right\} \qquad (27)$$

where P_i is as defined above, $k_{ij}(s)$ is the transition intensity between state i and state j under stress condition s, and $b_{ji}(s)$ is simply $a_{ji\omega}$ with $k_{ij}(s)$ substituted for k_{ij} and P_j substituted for $\langle A_n \rangle_\omega(0)$. The fact that the implicit function defined in this way exists follows from the fact that each side of Eq. (27) is an increasing function of t. The fact that each side of (27) is nondecreasing follows immediately from the fact that M is absorbing. To see that each side is increasing, it is sufficient to recall that $(d/dt)\langle M \rangle_\omega(t)$ has the form

$$(d/dt)\langle M \rangle_\omega(t) = \sum k_{im} \langle A_i \rangle_\omega(t)$$

where each k_{im} is nonnegative and at least one k_{im} is positive with the corresponding $\langle A_i \rangle_\omega(0)$ positive.

From the proof of the above theorem and particularly Eq. (27), the following corollary is immediate.

Corollary. For simple statistical kinetic models satisfying assumptions 1–3, the corresponding acceleration transforms have precisely the same form as those derived from systems of deterministic differential equations assuming random initial conditions.

Example 4, the stochastically coupled model, provides a counterexample of the conjecture that this result holds in general.

To see what form these transforms can take, we now examine transforms defined by the examples given in Section 2.

Example 3.1. Acceleration Transform for a One-Step Process

From Eqs. (10) and (27) we see that the acceleration transform for the simple single-step process may be derived from

$$1 - \exp[-k_1(s_1)t_1] = 1 - \exp[-k_1(s_2)t_2]$$

which reduces to

$$t_1 = \theta t_2 \tag{28}$$

where $\theta = k_1(s_2)/k_1(s_1)$. In the reliability field, this model is known as the accelerated life model,[5] where θ is an acceleration factor. The main point to notice is that the k_{ij} will not be recoverable directly from the transform, even in this simple case.

Remark 3. In the situation where the degradation process is limited by a chemical reaction, $n_\omega > 10^{20}$, the accelerated life model can be shown to hold for second- and higher order reactions as long as the reaction has only a single step.

Example 3.2. Acceleration Transform for a Simple Sequential Process

From Eq. (14) we see that as long as assumption 3 holds, we can defined $P = \langle A \rangle_\omega(0)/n_\omega$ so that the acceleration transform between stress conditions s_1 and s_2 is implicitly defined by the equation

$$P\left\{1 + \frac{k_1(s_1)}{k_2(s_1) - k_1(s_1)} \exp[-k_2(s_1)t_1] - \frac{k_2(s_1)}{k_2(s_1) - k_1(s_1)} \exp[-k_1(s_1)t_1]\right\}$$

$$+ (1-P)\{1 - \exp[-k_2(s_1)t_1]\}$$

$$= P\left\{1 + \frac{k_1(s_2)}{k_2(s_2) - k_1(s_2)} \exp[-k_2(s_2)t_2] - \frac{k_2(s_2)}{k_2(s_2) - k_1(s_2)} \exp[-k_1(s_2)t_2]\right\}$$

$$+ (1-P)\{1 - \exp[-k_2(s_2)t_2]\} \tag{29}$$

This example is of interest for several reasons. First, the result requires the explicit use of assumption 3, an assumption that may restrict the applicability of the result. The general transform for this particular model, where $\langle A \rangle_\omega(0)/n_\omega$ varies with ω, can be written only as an implicit equation defined by integrals. Second, the function taking t_2 to t_1 can only be defined implicitly; there is no explicit form for it. Finally, all of the k_i are recoverable from the transform along with P. Thus, in this case the transform yields nearly complete information on the degradation process.

Example 3.3. Acceleration Transform for a Competing Process Model

Equations (15) and (27) imply that the transform for this model can be derived from

$$\frac{k_1(s_1)}{k_1(s_1) + k_2(s_1)} (1 - \exp\{-[k_1(s_1) + k_2(s_1)]t_1\})$$

$$= \frac{k_1(s_2)}{k_1(s_2) + k_2(s_2)} (1 - \exp\{-[k_1(s_2) + k_2(s_2)]t_2\}) \qquad (30)$$

which reduces to

$$1 - \exp(-\theta_1 t_1) = \theta_2 [1 - \exp(-\theta_3 t_2)] \qquad (31)$$

where

$$\theta_1 = k_1(s_1) + k_2(s_1)$$

$$\theta_2 = \frac{k_1(s_2)[k_1(s_1) + k_2(s_1)]}{[k_1(s_2) + k_2(s_2)] k_1(s_1)}$$

$$\theta_3 = k_1(s_2) + k_2(s_2)$$

An explicit function for the transform is defined by

$$t_1 = \frac{-\ln\{1 - \theta_2[1 - \exp(-\theta_3 t_2)]\}}{\theta_1} \qquad (32)$$

Equation (31) illustrates a curious property shared by acceleration transforms of statistical kinetic models with more than one absorbing state. Notice that if $\theta_2 < 1$, then there exist t_1 with no equivalent t_2, and if $\theta_2 > 1$, there exist t_2 with no equivalent t_1. In the former case, one would expect a lower proportion of units failing under condition s_2 than under s_1, and in the latter case, the reverse. This phenomenon of having a changing proportion of units fail with changing conditions is fairly common in accelerated life tests. This model allows for estimation in such a system, and also offers a testable interpretation. If the model is strictly true (no reversibility between states), then a large proportion of units surviving long exposure to low-stress conditions should take longer to fail when exposed to high stress than the equivalent tail of the distribution of new units.

Example 3.4. Acceleration Transforms for the Stochastically Coupled Model

The assumption used to construct acceleration transforms from simple statistical kinetic models will not produce convenient forms for stochastically coupled models because of the inherent nonlinearity. For our example, it is possible to eliminate the functional dependence of $P(\delta \in M: t, \omega \mid \delta \in C: 0, \omega)$ on ω only by assuming $\langle A \rangle_\omega(0) \simeq \langle A \rangle_0$, some constant independent of ω. We now examine the transforms that arise from this model under two situations. We first consider the case when $\langle A \rangle_\omega(0)$ is only moderately large and formula (24) holds. Then we consider the case in which $\langle A \rangle_\omega(0)$ is very large and formula (26) holds. The surprising result is that the acceleration transform for the former case provides more information about the degradation process than the acceleration transform for the latter case, even though intuition indicates that the process in the former situation is inherently more random than in the latter. In this section we explicitly denote the dependence of $\sigma^2(t)$ on S by writing $\sigma^2(t, s)$.

The transform for the first situation is the implicit relationship between t_1 and t_2 derived from

$$
\begin{aligned}
1 - \exp\Bigg[& -k_2(s_1)\langle A \rangle_\omega(0) \left(t_1 - \frac{1 - \exp[-k_1(s_1)t_1]}{k_1(s_1)} \right) \\
& - \frac{k_2^2(s_1)\langle A \rangle_\omega(0)}{k_1^2(s_1)2}\, \sigma^2(t_1, s_1) \Bigg] \\
= 1 - \exp\Bigg[& -k_2(s_2)\langle A \rangle_\omega(0) \left(t_2 - \frac{1 - \exp[-k_1(s_2)t_2]}{k_1(s_2)} \right) \\
& - \frac{k_2^2(s_2)\langle A \rangle_\omega(0)}{k_1^2(s_2)2}\, \sigma^2(t_2, s_2) \Bigg]
\end{aligned}
$$

which reduces to

$$
\begin{aligned}
k_2(s_1) & \left(t_1 - \frac{1 - \exp[-k_1(s_1)t_1]}{k_1(s_1)} \right) + \frac{k_2^2(s_1)}{k_1^2(s_1)2}\, \sigma^2(t_1, s_1) \\
= k_2(s_2) & \left(t_2 - \frac{1 - \exp[-k_1(s_2)t_2]}{k_1(s_2)} \right) + \frac{k_2^2(s_2)}{k_1^2(s_2)2}\, \sigma^2(t_2, s_2)
\end{aligned}
$$

Notice, given the definition of $\sigma^2(t, s)$ provided by (25), that all four of the transition intensities can be recovered directly from the acceleration transform. This result can be contrasted to the situation in which (26) holds, for

example, when a system of deterministic differential equations is appropriate, in which case the transform can be reduced to the form

$$t_1 - \frac{1 - \exp(-\theta_1 t_1)}{\theta_1} = \theta_2 \left(t_2 - \frac{1 - \exp(-\theta_3 t_2)}{\theta_3} \right)$$

where $\theta_1 = k_1(s_1)$, $\theta_2 = k_2(s_2)/k_2(s_1)$, and $\theta_3 = k_1(s_2)$. More complex stochastically coupled models will result in several approximate transforms depending on the initial number of flaws in each state. In particular, we see that the corollary to the theorem given in this section must be generalized with care, and sometimes acceleration transforms can be used to help identify the kinds of flaws causing degradation, by providing information on their abundance.

4. DISCUSSION

Acceleration transforms were derived as new models of accelerated life test data[1] by assuming that some of the mathematical models normally used in elementary chemical kinetics were good approximations to degradation processes. In ref. 1 we demonstrated that:

1. The commonly used accelerated life model could be derived as the acceleration transform for the simplest physical model.

2. For one example where the accelerated life model did not fit well, a slightly more complex acceleration transform did fit well, and it both extrapolated better to field data than the acceleration factor model and generated valid qualitative predictions about the behavior of the material system.

It was the second point that in large part motivated the work in this paper. Acceleration transforms, combined with statistical methods of selecting and estimating models from data, provide a tool for making inductions about the processes occurring in a material while it is degrading. Ignoring for the moment the problems introduced by statistical estimation[6] and assuming that the acceleration transform fitting the data is chosen correctly, then, in order for induction to proceed intelligently, it is necessary to understand the broad range of possible models corresponding to a single acceleration transform. While the work presented here does not completely cover that range, it does expand the range previously covered. The postulates were motivated by the desire to approximate such diverse phenomena as nth-order chemical reactions [which can be done through appropriate definition of $k_{ij}(D_\omega(t))$] and crack initiation and propagation, in which the distribution of energy throughout the system changes as soon as a crack begins to form.

The main contribution of this paper is thus the theorem in Section 3 and its corollary, and the postulates and assumptions leading to it. These provide a set of sufficient conditions, stated in terms of physical properties of the material systems and their environments, for acceleration transforms to provide a valid explanation of the way failure distributions change as stress level changes. These sufficient conditions are broad enough so that the scientist/data analyst knowing them will understand how much and how little the use of acceleration transforms has permitted understanding of the processes occurring in the material system being studied. Proper fitting of the θ terms as functions of the environment may then supply further information.

In conclusion, this paper supplies a self-consistent portion of a theory on which to base the study of degradation phenomena using accelerated life testing. The postulates and assumptions are too restrictive to provide a theory for all degradation phenomena, but the success of the accelerated life model in combination with the Arrhenius model of temperature dependence, and our success with the one example,[1,6] indicate that there are material systems that can be well approximated by these postulates.

The work done here only represents a beginning. Example 4 in Sections 2 and 3 demonstrates that there are several phenomena that may be described through acceleration transforms and statistical kinetics that are not covered by Theorem 1. Modifying A3 will allow for distinct subpopulations. More work must also be done on experiment design and data analytic estimation procedures and on developing both physical and data analytic strategies that fully take advantage of the link these models provide between the physical analysis of degradation processes and the statistical analysis of accelerated life test data. Also, the extension of statistical kinetics to allow reversible processes and the use of a quantum mechanical description of the probability mechanism might greatly expand its applicability.

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