A simple function for the description of near-exponential decays: The stretched or compressed hyperbola

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The modeling of systems that exhibit near-exponential decay is most commonly done using a sum of exponentials or a stretched exponential. We note some drawbacks of these representations and present an alternative model, the stretched or compressed hyperbola, first described by E. Becquerel in the 1860s. This representation might be more helpful for interpolation, extrapolation, and classification of decays and requires only one additional parameter compared to simple exponential decay.

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I. INTRODUCTION

This paper concerns the well-known phenomenon of decay, in which a quantity of interest gradually decreases to zero as a function of time or distance. There are many different types of decay, but one in particular is mathematically simple and intriguing; it arises when the rate of decrease of the quantity is proportional to the quantity itself,

$$\frac{dI}{dt} = -kI, \tag{1}$$

which has the well-known exponential decay solution:[1,2]

$$I(t) = I(0)e^{-kt}. \tag{2}$$

A common scenario for such a decay involves a very large number of independent entities, each having a constant probability per unit time of changing form.

Such simple decay characteristics are rarely realized. Most decays are more complex, and this complexity manifests itself in nonexponential decay. In this paper we are primarily interested in situations for which the departure from exponential is too much to ignore, but is describable by a modest departure from exponential decay.

Deviation from exponential decay is especially evident if we plot $\ln(I)$ versus t, because only exponential decay results in a straight line in such a plot. As an example, Fig. 1 shows the decay of the electrical potential difference in two simple electrical circuits in which the switch is closed at $t=0$ commencing a decay of the voltage toward zero. For circuit (a) the plot is the straight line associated with exponential decay, and for circuit (b) it is clearly not.

Although the electrical circuit (b) is more complex, it is straightforward to determine the functional form of the decay. Even if we did not know the values of one or more of the components in the circuit, it would take only a few measurements to have enough data to determine these parameters and thus have a useful characterization of this more complex system.

In real systems it is common not to have detailed knowledge of the functional decay mechanism, but only to observe that the decay is approximately, but not exactly, exponential. Examples include decays involving light guides[3] and luminescence,[4] but more generally any complex system that exhibits decay has the potential to be in this category. The phenomenon of decay is ubiquitous; it is observed in any system transitioning from a nonequilibrium state toward equilibrium, and with any quantity that decreases over distance or time. Decay is found in the physical and biological sciences, medicine, education, business, economics among many other fields. Deviations from Eq. (1) can occur for many reasons such as the dependence of the decay parameter k on I, and a variety of decaying subpopulations with a diversity of k values. Often, we have no information about such details other than that provided by the decay data.

There are three main reasons that fitting a simple function to the observed decay can be useful. One is interpolation. Often measurements are difficult and only a few can be made, and there is a need to estimate the value of the quantity between measurements. Sometimes, it is important to use extrapolation to make an educated guess about the future value of a quantity, given its decay history. In the absence of a model this procedure necessarily involves some degree of uncertainty. It also might be helpful to characterize a given decay process according to the degree to which it deviates from a simple exponential decay. In such cases it would be helpful to have a simple and easily determined measure of this degree of deviation.

For each of these reasons it is desirable to fit the data with a function that is simple and easy to use, and which works well for interpolation, prediction, and classification.

The goal of this paper is to provide a useful mathematical function for treating such situations. A form of this little known function was first described in the 1860s by the physicist Edmond Becquerel (discoverer of the photovoltaic effect and father of Henri Becquerel, the discoverer of radioactivity) for interpreting phosphorescence intensity decay data.[5] Becquerel used his phosphoroscope to measure the

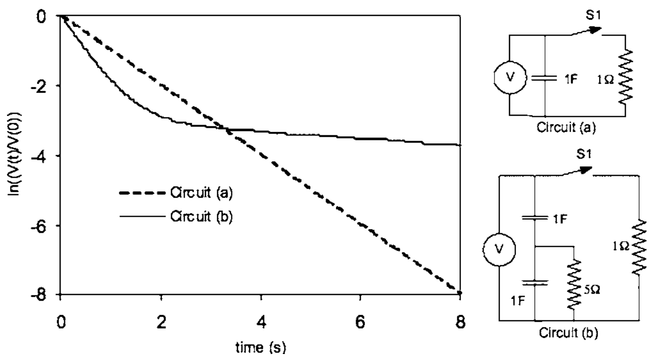

Fig. 1. Decay plots for two simple electrical circuits.

luminescence decay of various compounds. To analyze some of his results he used a general empirical equation,[5] which satisfies the relation $I(t)^m(t+a)=a$ and has the form

$$I(t) = \frac{1}{(1+t/a)^{1/m}}, \tag{3}$$

with $m<1$ and a a parameter with dimensions of time. Here we use a variant of this function that has a more intuitive connection to exponential decay.

II. DEVIATION FROM EXPONENTIAL DECAY

The most popular method for fitting nonexponential decay curves is to use a sum of exponentials.[6] This approach is valuable when a model predicts a sum of exponentials, but otherwise such a sum contains many free parameters (for example, five for a sum of three exponentials) lacking physical significance.

We propose another approach, which has two important characteristics. The first is that the function be versatile and do a reasonable job of interpolation, extrapolation, and classification. The second, which to some extent is a consequence of the first, is that it should have a minimum number of free parameters. If exponential decay is normalized to be one at $t=0$ and approaches zero for long times, then it is parameterized by one free parameter. Ideally, the simplest fit for nonexponential decay would add just one more parameter.

One approach to slightly more complex exponential decay is to modify the decay equation by adding one or more adjustable parameters. Two popular examples are the biexponential function[2,5,6] and the stretched exponential function.[7–10] Assuming that $I(0)=1$, these are given by

$$I(t) = ae^{-k_1 t} + (1-a)e^{-k_2 t}, \tag{4}$$

$$I(t) = e^{-(kt)^c}. \tag{5}$$

These functions are useful in some contexts, but have problems, which limit their use in many settings. The biexponential introduces two new parameters, and both functions may behave unnaturally for large values of t. A different approach, as described in the following is to make a modest change not to the decay function, but to the differential equation for which the decay function is a solution.

III. A SMALL MODIFICATION TO THE DECAY DIFFERENTIAL EQUATION

Exponential decay can also be written as

$$I(t) = I(0)e^{-t/\tau}, \tag{6}$$

where the lifetime $\tau = 1/k$ is a constant.

For nonexponential decay we expect that τ might depend on time. Equation (1) can be formally integrated to give

$$I(t) = I(0)\exp\left[-\int_0^t \frac{dt}{\tau(t)}\right]. \tag{7}$$

This result is completely general but is not useful because $\tau(t)$ is not specified. If we consider the power series expansion of $\tau(t)$,

$$\tau(t) = \tau(0) + c_1 t + c_2 t^2 + \ldots, \tag{8}$$

an approximate decay function can be obtained by truncating the expansion at order n. Truncation to first-order yields

$$\tau(t) = \tau(0) + ct, \tag{9}$$

where c is an additional (dimensionless) parameter. Usually, τ increases with time, and hence $c>0$.

Equation (7) can be readily solved within this approximation. The solution with $I(0)=1$ is

$$I(t) = (1+kct)^{-c^{-1}} \quad \text{for } c>0,$$

$$I(t) = e^{-kt} \quad \text{for } c=0. \tag{10}$$

According to Eq. (10) the value of k is $1/\tau(0)$. Note that for sufficiently long times Eq. (10) depends on time as a power law.

As will be apparent in the examples discussed in Sec. IV, the value of c represents the extent to which a decay function deviates from exponential. It is easy to show numerically that c^2 is approximately the mean square fractional error in fitting $I(t)$ by a simple exponential over the first 98% of the decay.

Equation (10) is equivalent to Becquerel's decay function, and is a compressed hyperbola for $c<1$ and a stretched hyperbola[11] for $c>1$. The acronym DHARA is suggested for this mathematical expression because the function in Eq. (10) is the derivative of the well-known utility function used in risk aversion known as the hyperbolic absolute risk aversion function (HARA) (Ref. 12). The form shown in Eq. (10) has the advantage that the constant k is analogous to the decay coefficient in purely exponential decay; in both cases k is the fractional decay rate at $t=0$. It does not diverge as c approaches zero, which can be helpful when fitting a decay curve by means of iterative adjustment of the parameters k and c.

IV. EXAMPLES OF THE USE OF THE DHARA FUNCTION FOR FITTING DECAY DATA

A. Hollow light guide flux decay

The propagation of light in hollow light guides is a good example of a continuous mixture of entities with various decay rates. In this case the entities are light rays that have a certain angular deviation from the guide axis. The greater the deviation, the greater the rate of interaction with the wall of the light guide, and hence the greater the rate of decay per

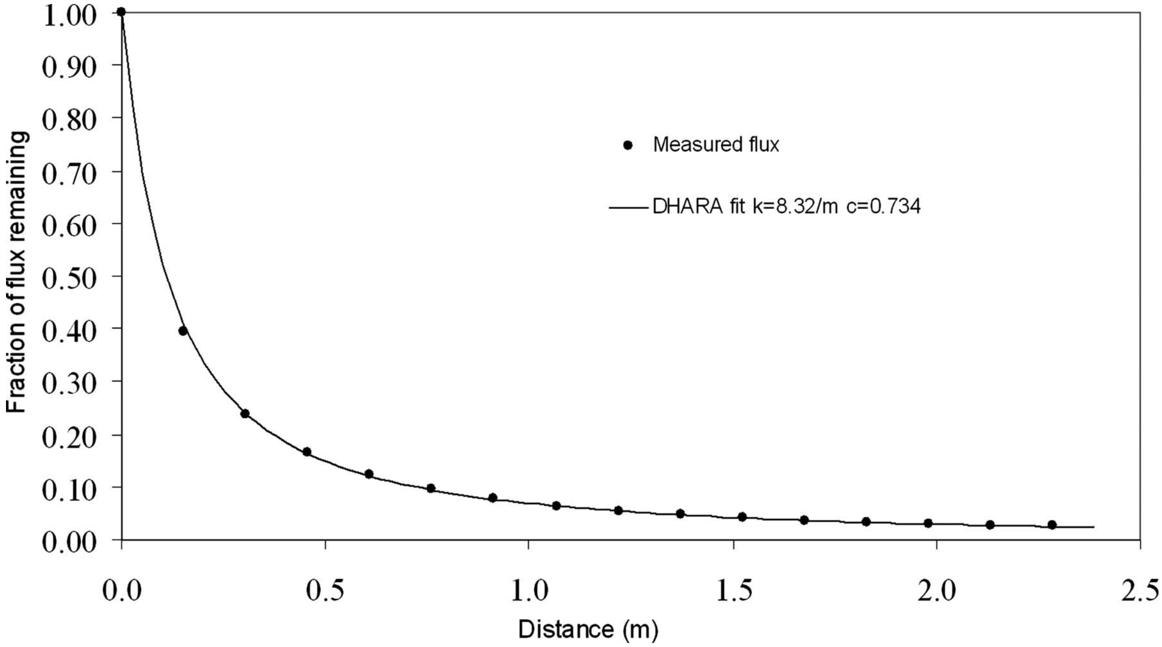

Fig. 2. Decay of luminous flux versus distance down a rough metallic pipe.

unit length down the guide.[3] This simple interpretation is only partially correct because light rays may change their angular deviation from the guide wall as a function of distance, and generally the overall behavior will depend on the original directional distribution of rays' which is usually not known. Nevertheless, even in the most nonideal case the DHARA function appears to work well. Figure 2 shows the fraction of the original flux measured as a function of distance down a 0.05 m diameter cylindrical pipe of unfinished aluminum; the source is a commercial 50 W incandescent reflector lamp. As can be seen, there is a good fit to a DHARA function with $k=8.3\pm0.2\ \mathrm{m}^{-1}$ and $c=0.73\pm0.02$.

B. Luminescence decay

In his original studies of luminescence decay, Becquerel employed the function shown in Eq. (3), which is formally identical to the DHARA function, Eq. (10), with $a=1/kc$ and $m=c$. This nonexponential form of the luminescence decay of phosphors is accounted for by trapping and retrapping processes. There is an underlying distribution of decay times due to a distribution of traps with different depths.[4] The DHARA function provides satisfactory fits to the luminescence decay of phosphors.[13–15] The luminescence intensity decay of a sample of green glowing strontium sulfide is shown in Fig. 3 (a selection of original Becquerel data, taken from Ref. 5, pp. 293–294). As can be seen, the DHARA function with $k=0.67\pm0.01\ \mathrm{s}^{-1}$ and $c=0.877\pm0.007$ provides a good fit that spans more than 3 orders of magnitude in intensity.

Becquerel's fit to the long-time portion of the decay (25–80 min) yielded slightly different parameters ($k=0.438/\mathrm{s}$, $c=0.806$), which he used to extrapolate the intensity to 30 h when the faint emission of the sample was still visible to the naked eye but too weak to be quantified. He obtained a relative intensity of 2×10^{-6} at this time. By taking into account the relation between the initial emission intensity and the intensity of a candle, and the relation between the intensity of a candle and the intensity of ambient light in a sunny day, he concluded that the human eye was sensitive to a range of light intensities spanning at least 11 orders of magnitude,[5] an estimate that is in remarkably good agreement with present knowledge.

Other examples of the use of the DHARA function in photophysics can be cited. Wlodarczyk and Kierdaszuk[16] found that the DHARA function provides good fits of fluorescence decays, implying a narrow distribution of decay times approximated by the gamma distribution. They also used the DHARA function to analyze luminescence decay when triplet excitation transport occurs in disordered organic solids.[17] This function was also successfully used for describing the decay of delayed fluorescence resulting from triplet-triplet annihilation in polyphenylquinoxalines in frozen solutions or films.[18]

An upper limit for the parameter c exists for luminescence decays. It cannot be higher than unity, otherwise the integrated intensity diverges.[4] Therefore, only the compressed hyperbola is relevant in this context.

We remark that, once illuminated, a great variety of biological systems emit a very weak delayed luminescence whose decay can be modeled by the DHARA function.[19–21]

C. Stress decay in biological fibers

This example concerns the time dependence of the stress-strain relation in polymeric materials. In Ref. 22 a fiber of spider dragline silk was subjected to a rapid, substantial strain at time zero, and the resultant stress was observed over time. A portion of the stress decays away leaving a residual stress $S_{\min}$. Figure 4 shows the fraction that remains as a function of time. As shown, the decay curve can be fit well by a DHARA decay function with $k=0.045\pm0.002\ \mathrm{s}^{-1}$; the remarkably large value of $c=3.45\pm0.07$ accounts for the long tail in the decay.

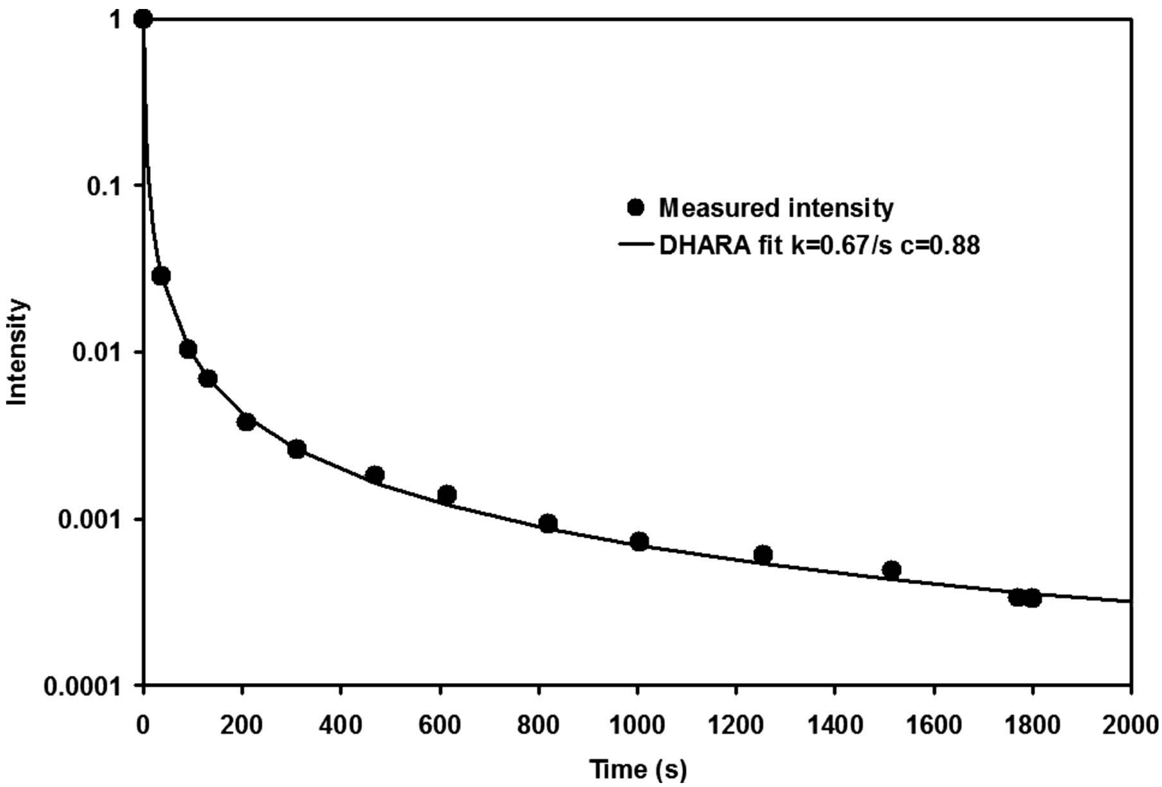

Fig. 3. Phosphorescence intensity decay of strontium sulfide (original Becquerel's data) (Ref. 5). Note that the fit spans more than 3 orders of magnitude in intensity.

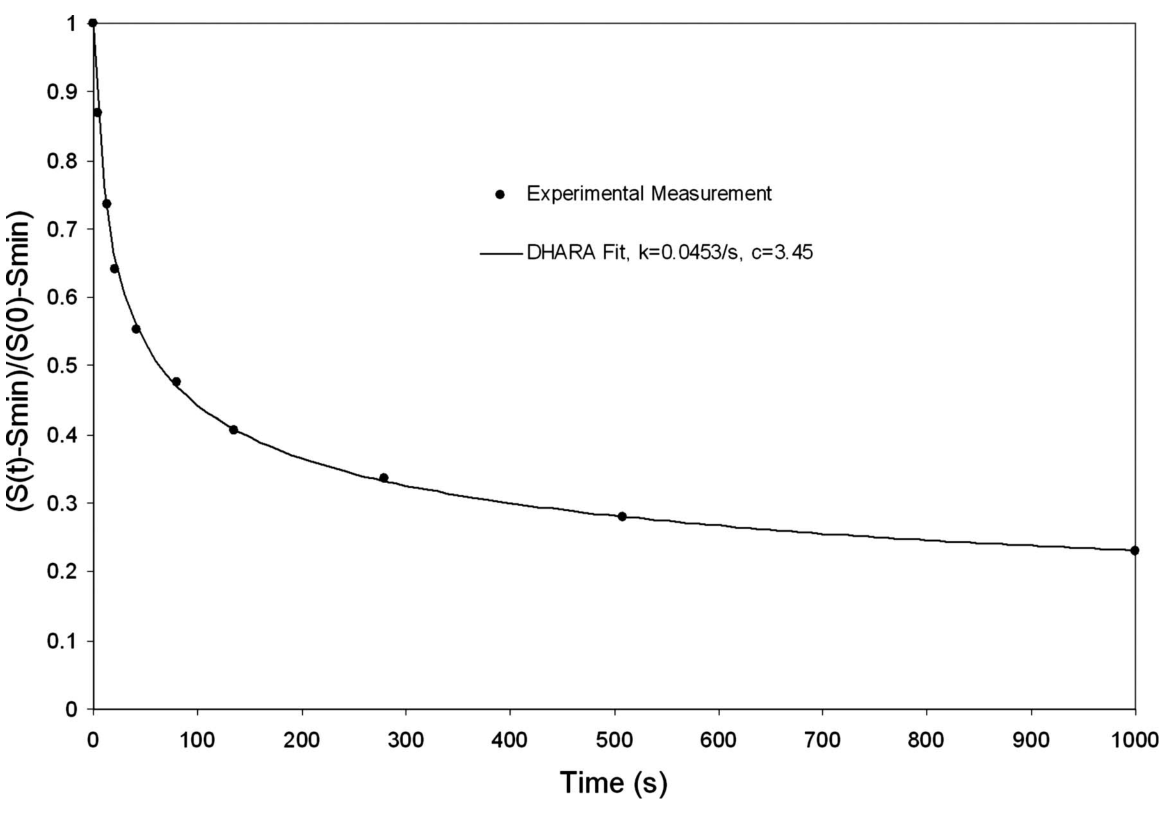

Fig. 4. Decay of residual stress in spider silk, fitted with DHARA.

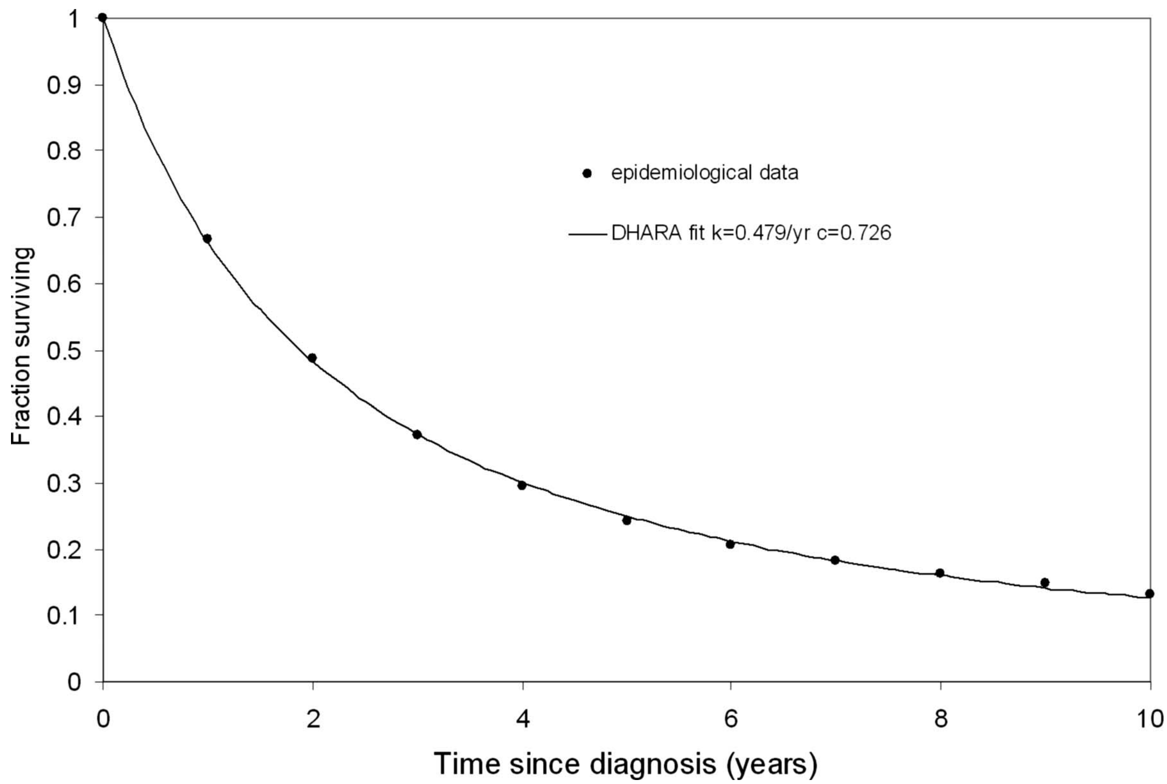

Fig. 5. Survival rates for distant stage metastatic breast cancer.

D. Cancer survival rate decay

We fitted the survival rates as a function of the number of years since diagnosis for various forms of cancer, based on available epidemiological data.[23] Figure 5 shows the fitted DHARA fit of distant stage metastatic breast cancer with $k = 0.48 \pm 0.01\ \mathrm{yr}^{-1}$, and $c = 0.73 \pm 0.03$. This example illustrates a case where using DHARA for predictive purposes may be helpful. If a new treatment modality is underway, only results up to a certain point of time are available, and it might be very helpful to extrapolate to estimate quickly as to whether the results are tracking toward an improvement in long term survival. As mentioned, extrapolation results should be used carefully in the absence of a physical model.

E. Wood moisture content decay

As a further test of the applicability of the DHARA function, we did a simple test of the drying of wood. We used a 2.5 cm cube of kiln dried hemlock wood, weighed it, and soaked it in water for 24 h. The weight of the wood increased by about 50% as a result. The wood was then allowed to dry through exposure to air at approximately 20 °C at a relative humidity of approximately 50%. Its weight was periodically monitored, and the fractional retention of the added moisture was calculated.

Figure 6 shows the results of this investigation. The fractional remaining moisture content decays over time, and is fit well by a DHARA function with $k = 0.055 \pm 0.0008\ \mathrm{h}^{-1}$ and $c = 0.20 \pm 0.02$.

In selecting these examples we looked for a variety of practical cases for which moderately nonexponential decay is anticipated. The DHARA function has the potential to be useful in many settings, which leads to the interesting question of when and why the DHARA function should be a useful fit.

V. ALTERNATIVE DERIVATION

It is straightforward to demonstrate that the DHARA function is not a perfect model for all near-exponential decays. For examples the nonexponential decay circuit (b) shown in Fig. 1 exhibits a biexponential decay which can at best only be approximated by the DHARA function. The limitations of the DHARA function can be traced back to the fact that it results from a series expansion truncated to the first-order, Eq. (9). It is interesting to consider whether there is a class of decay conditions for which this function fits perfectly, and if these conditions approximate a realistic range of typical conditions. To do so we introduce some notation. Consider the case of a large number of decaying entities exhibiting a distribution of decay times. We can classify each decaying entity according to its individual decay time τ or by its decay rate k. At time t let $d(\tau,t)$ be the density of entities with decay time τ. The intensity of each entity decays exponentially with time such that

$$d(\tau,t) = d(\tau,0)\exp(-t/\tau). \tag{11}$$

Thus the intensity $I(t)$ at any time is given by the integral

$$I(t) = \int_0^\infty d(\tau,0)\exp(-t/\tau)d\tau = \int_0^\infty f(k,0)\exp(-kt)dk, \tag{12}$$

where $f(k,0)$ is the probability density of the decay rates. The decay function $I(t)$ is thus the Laplace transform of

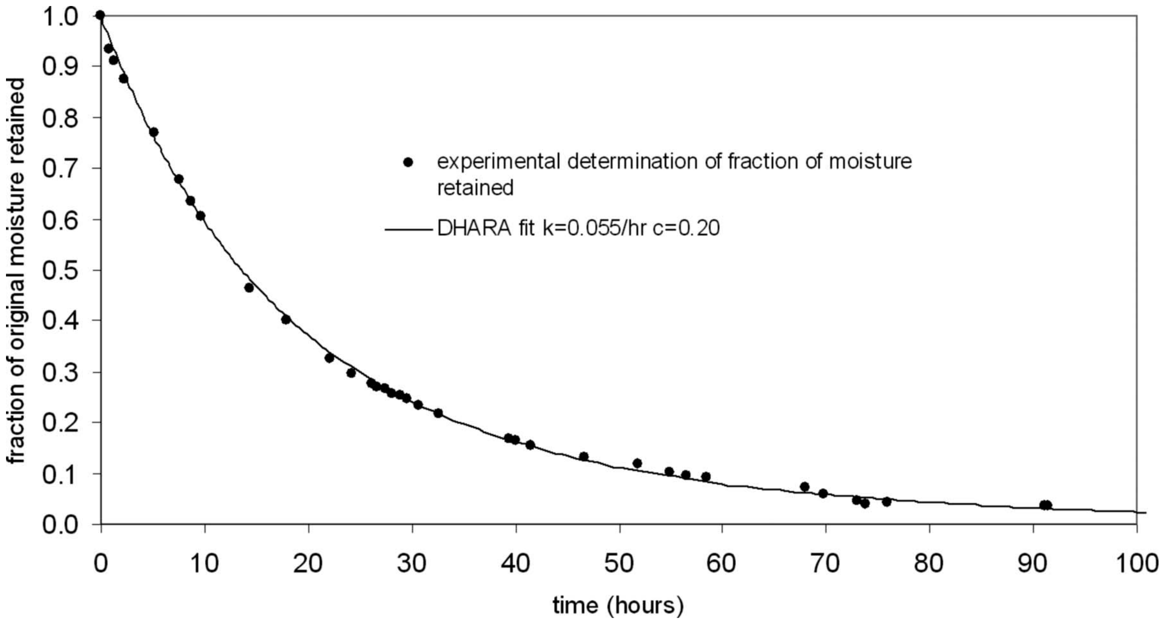

Fig. 6. Decay of fractional moisture retention in wood.

$f(k,0)$. If $I(t)$ is the DHARA function, then $f(k,0)$ is given by

$$f(k,0) = \frac{\alpha}{\Gamma(1/c)}(\alpha k)^{(1/c)-1}\exp(-\alpha k), \tag{13}$$

with $\alpha = \tau(0)/c$. The analogous probability density function of lifetimes $d(\tau,0)$ can also be obtained. Equation (13) is known as the gamma probability density function in statistics.[24] As shown in Fig. 7, Eq. (13) is a plausible distribution function because it can closely approximate an actual distribution for a wide range of situations ranging from very narrow ($c \approx 0$) to very broad ($c \approx 1$) distributions, or to distributions with a steep decay from $k=0$ ($c \gg 1$). The coefficient of variation (the ratio of the standard deviation to the mean) of the probability density function is $\sqrt{c}$. From this perspective it is not surprising that this simple model works well in a variety of settings.

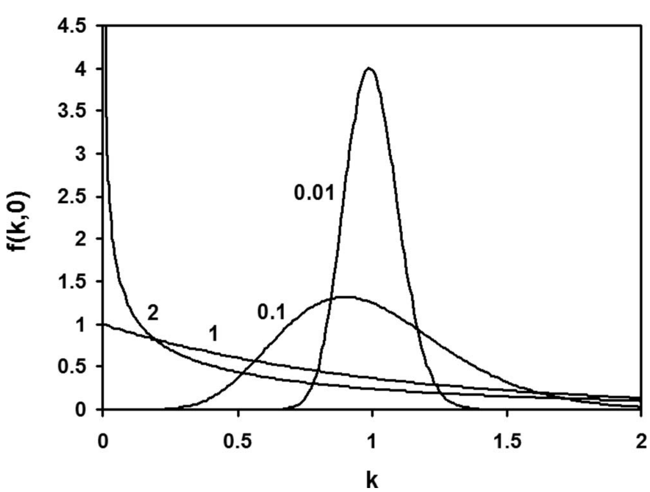

Fig. 7. Examples of decay density functions that yield exact DHARA decay ranging from narrow to broad to decaying density distributions. $\tau(0)=1$ in all cases. The number next to each curve is the respective value of parameter c.

VI. CONCLUSION

The stretched or compressed hyperbola, already used by E. Becquerel in the 1860s, is an easy to use, simple function for characterizing near-exponential decay in a wide variety of complex systems. An important advantage is that it is an exact solution to a common situation in which the instantaneous decay time changes at a constant, nonzero rate. This function has the advantage of mathematical simplicity, with just one dimensionless additional parameter compared to simple exponential decay. Most importantly, it works well in a wide variety of settings for interpolation, extrapolation, and classification of near-exponential decay. We recommend further work to identify decay situations that may benefit from this remarkably simple function. Possible areas for further research might be a variety of decay mechanisms in economics, psychology, and the life sciences, where the complexity of the systems limits the likelihood of a precise treatment of the underlying mechanisms for decay.

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