Photoconductor Discharge Curves, the Stretched Exponential, and Exponential Decay Functions

Eric Stelter, NexPress Solutions, Inc., Rochester, New York, USA

Abstract

Exponential decay, bi-exponential decay, and related decay processes are common in the physical world. Stretched exponential time dependence of the form $e^{-(kt)^c}$ *has been observed in connection with the discharge of electrophotographic photoconductors, luminescence in porous silicon, dielectric relaxation in glassy and polymeric materials, as well as in other systems. Exponential decay, the stretched exponential, the Kohlrausch-Williams-Watts function KWW, and the Buettner function satisfy a differential equation that depends on the exponent c and the entropy of the system. The form of the decay function determined by the exponent c can be shown to be consistent with cooperative events occurring during relaxation and can be related to the chemical potential of the system. This indicates that probabilistic, cooperative events may play a role in the dynamics of stretched exponential decay processes in addition to distributions of relaxation times and relaxation paths.*

Introduction

The Exponential and the Stretched Exponential

Exponential decay functions have the familiar form

$$f_{\exp}(t) = e^{-kt} \tag{1}$$

with rate constant k and satisfy a differential equation in which the rate of decay is proportional to the magnitude of $f_{\exp}(t)$.

$$\frac{\partial f_{\exp}(t)}{\partial t} = -k f_{\exp}(t) \tag{2}$$

The stretched exponential has the form

$$f(t) = e^{-(kt)^c} \tag{3}$$

Values of c <1 result in decay times that are longer than for exponential decay. The stretched exponential is plotted for c<1, c=1, and c>1 in Figure 1. The case c=1 reduces to the exponential function, Equation (1). Many physical systems are described by a stretched exponential with c<1 during relaxation, which is known as the Kohlrausch-Williams-Watts function (KWW).[1-2] Stretched exponential time dependence with c<1 in photoconductors was first observed by Merle Scharfe of Xerox in measurements of the transient photocurrent of amorphous As_2Se_3 as a function of time.[3] Albert Buettner, in work on the photodischarge of organic photoconductors begun at Eastman Kodak, observed that the photoconductor voltage as a function of exposure E for some organic photoconductors follows a stretched exponential with c>1.[4]

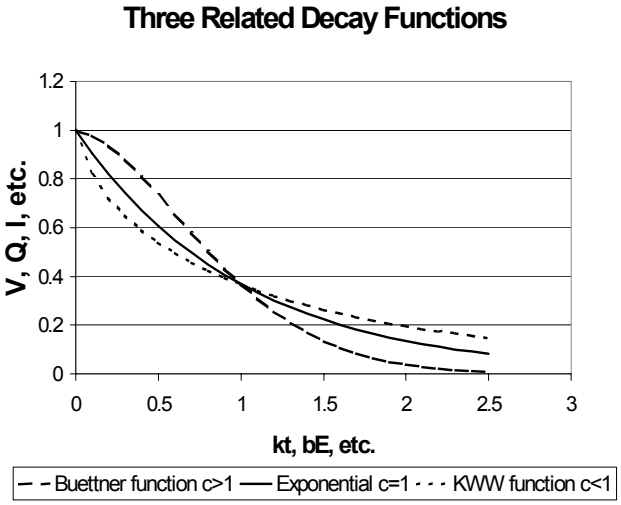
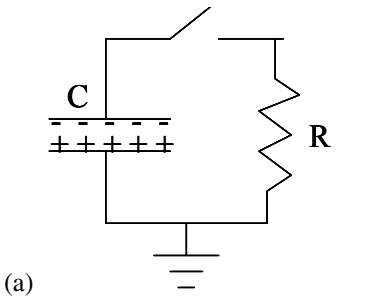


Figure 1. Three related decay functions. The stretched exponential with c<1 and c>1 compared to exponential decay with c=1.

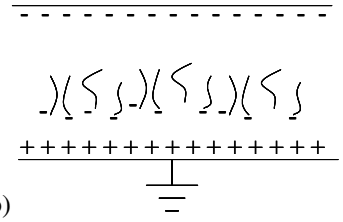
At long times, the KWW function with c<1 is greater than the exponential function, corresponding to slower decay, and the Buettner function with c>1 is less than the exponential, corresponding to faster decay. Most explanations of the behavior for c<1 or c>1 for photoconductors[5] and other systems assume that there is an *a priori* distribution of decay times or decay paths. The behavior for c<1 may also have a probabilistic component resulting from early decay events making later decay events less likely to occur. The behavior for c>1 may have a probabilistic component resulting from early decay events making later decay events more likely, similar to a log-jam for which removing a few logs makes the whole pile collapse.

Example Systems

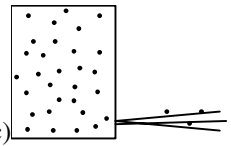
Model systems in which exponential or stretched exponential relaxation occur include a capacitor discharging through a resistor, a photoconductor discharging, and gas discharging from a pressurized vessel through a hole or membrane, as shown in Fig. 2.



(a)



(b)



(c)

Figure 2. Model systems (a) capacitor discharging through a resistor, (b) photoconductor discharging, and (c) gas escaping from a pressurized vessel.

These systems are in equilibrium until a switch is thrown, an exposure is made, or a valve is opened, which starts relaxation to another equilibrium state. Decay of the capacitor C is affected by the resistor R, decay of the photoconductor voltage is affected by the presence of traps, and the escape of the gas from the vessel is affected by the characteristics of the hole or membrane.

The Significance of c

Differential Equation for the Stretched Exponential

A general differential equation for decay can be written by eliminating constant k from Equation (2) with Equation (1).

$$t\frac{\partial f_{\exp}(t)}{\partial t} = f_{\exp}(t)\ln\left[f_{\exp}(t)/f_{\exp}(0)\right] \tag{4}$$

Although k does not appear explicitly as a constant in this equation, $f_{exp}(t) = Ae^{-kt}$ is a solution.

The stretched exponential $f(t) = e^{-(kt)^c}$ is a solution of the differential equation:

$$t\frac{\partial f(t)}{\partial t} = cf(t)\ln\left[f(t)/f(0)\right] \tag{5}$$

The differential equations for the stretched exponential and Equation (4) for exponential decay differ only by proportionality constant c. In the limit $c\rightarrow 1$, $f(t)\rightarrow f_{exp}(t)$ and both differential equations become identical. Both differential equations are linear: if $f(t)$ is a solution, then $Af(t)$ is also a solution. Of course, other variables can be substituted for t, such as exposure E.

Formulation in Terms of Entropy

The differential equation for the stretched exponential, Equation (5), can be rewritten as:

$$t\frac{\partial f(t)}{\partial t} = cf(t)\ln\left[f(t)\right] - cf(t)\ln\left[f(0)\right] \tag{6}$$

where $f(t)\ln\left[f(t)\right]$ has the form of a generalized entropy.[6] Assuming that the quantity being measured, such as photoconductor voltage or current, is related to the number of particles or charges N present in the portion of the system under consideration, with $N>>1$ initially, then for N distinguishable particles or decay paths the fundamental entropy $S_F(N)$ is the natural logarithm of the number of accessible states:[7]

$$S_F(N) = \ln(N!) \approx N\ln(N) \tag{7}$$

resulting in:

$$\frac{\partial f(t)}{\partial t} = -\frac{c}{tN_0}\left[f(t)S_F(0) - S_F(t)\right] \tag{8}$$

where the conventional entropy S and the fundamental entropy S_F are related by $S = k_B S_F$, $S_F(0)$ is the initial entropy $N_0 ln(N_0)$ of the portion of the system under consideration, or the subsystem, $N(t) = N_0 f(t) = N_0 e^{-(kt)^c}$, and $S_F(t)$ is the entropy that this portion of the system would reach if stopped at time t. Although the entropy of the entire system will increase or possibly remain unchanged, the entropy of the subsystem that is relaxing will typically decrease as particles or charges leave and it approaches a simpler configuration. For example, discharging a capacitor through a resistor increases the entropy of the system due to heating of the resistor, but the entropy of a discharged capacitor is less than that of a charged capacitor.

Transition Probabilities and c

The probability $p(t)$ that a single particle will decay or leave the subsystem is given by equation

$$p(t) = \frac{\left|\frac{\partial N(t)}{\partial t}\right|}{N(t)} = \frac{c}{t}\left|\ln\left[N(t)/N(0)\right]\right| \tag{9}$$

for $N(t) = N_0 f(t) = N_0 e^{-(kt)^c}$. The absolute value signs are required to make $p(t)$ positive, as probabilities are between 0 and 1. Note that for exponential decay with c=1 for a system described in terms of the number of particles in the system, $p(t)=k$. Defining fundamental entropy per particle $s_F = S_F/N \approx ln(N)$, the transition probability at t=0 can be found from:

$$p(t) = \frac{c}{t}\left|\left[s_F(N(t)) - s_F(N(0))\right]\right| \tag{10}$$

$$p(t) = c\left|\left[\Delta s_F(N(t))/\Delta t\right]\right|$$

and, in the limit $\Delta t \to 0$,

$$p(t)\big|_{t=0} = c\left|\frac{\partial s_F(t)}{\partial t}\right|_{t=0} \tag{11}$$

The transition probability at t=0 for a particle to leave the subsystem is c times the magnitude of the rate of change per unit time of the fundamental entropy per particle.

The Chemical Potential and c

In a physical system where the distribution of the number of states as a function of energy is determined by temperature T, (in other words, for most microscopic systems) the behavior at t=0 can be used to estimate thermodynamic quantities, such as the chemical potential. The chemical potential is related to the fractional change of the number of accessible states with a change in the number of particles, and the chemical potential μ is defined as:[8]

$$-\frac{\mu}{k_B T} \equiv \left.\frac{\partial S_F}{\partial N}\right|_{U,V} \tag{12}$$

Using:

$$\frac{\partial S_F}{\partial N} = N\frac{\partial s_F}{\partial N} + s_F \tag{13}$$

the chemical potential can be rewritten as:

$$\mu = -k_B T\left[N\frac{\partial s_F(t)}{\partial N} + s_F(t)\right]_{t=0} \tag{14}$$

The derivative $\partial s/\partial N$ can be evaluated from the transition probability, Equation (11)

$$p(t)\big|_{t=0} = c\left|\frac{\partial s_F}{\partial N}\frac{\partial N}{\partial t}\right|_{t=0} = \left|\frac{\partial N}{\partial t}\Big/ N\right|_{t=0} \tag{15}$$

yielding:

$$\left|\frac{\partial s_F}{\partial N}\right|_{t=0} = \left.\frac{1}{cN}\right|_{t=0} \tag{16}$$

Removing the absolute value signs, it is required, as c>0 and N>0, that:

$$\partial s_F\big|_{t=0} = \left.\frac{1}{cN}\partial N\right|_{t=0} \text{ for } \left.\frac{\partial s_F}{\partial N}\right|_{t=0} > 0 \tag{17}$$

and

$$\partial s_F\big|_{t=0} = -\left.\frac{1}{cN}\partial N\right|_{t=0} \text{ for } \left.\frac{\partial s_F}{\partial N}\right|_{t=0} < 0 \tag{18}$$

The chemical potential μ can be expressed in terms of c as:

$$-\frac{\mu}{k_B T} = \left[\frac{1}{c} + s_F(t)\right]_{t=0} \text{ for } \left.\frac{\partial s_F}{\partial N}\right|_{t=0} > 0 \tag{19}$$

and

$$-\frac{\mu}{k_B T} = \left[-\frac{1}{c} + s_F(t)\right]_{t=0} \text{ for } \left.\frac{\partial s_F}{\partial N}\right|_{t=0} < 0 \tag{20}$$

Example System: The Ideal Gas

An extremely general form of entropy has been used in the preceding, motivated by the desire to explain the behavior of systems (photoconductors) with c<1 and c>1. The ideal gas provides an opportunity to examine another "real" system.

Particles Escaping from a Pressurize Vessel

A monoatomic ideal gas in a pressurized vessel escaping slowly at constant T through a small hole, as shown in Figure 2 (c) has no structure and any particle has an equal probability of escaping. Consequently, it is expected that the number of particles in the vessel, or the pressure, for example, will decrease exponentially with time and that c=1. The entropy $S_F(N,T,V)$ of a monoatomic ideal gas is given by the Sackur-Tetrode equation[9]

$$S_F(N,T,V) = N\ln\left[\left(\frac{mk_B T}{h^2/2\pi}\right)^{\frac{3}{2}}\left(\frac{V}{N}\right)\right] + \frac{5}{2}N \tag{21}$$

and, from Equation (11) for $\mu/k_B T$,

$$\left.-\frac{\mu}{k_B T}\right|_{t=0} \equiv \left.\frac{\partial S_F}{\partial N}\right|_{t=0} = -1 + s_F \tag{22}$$

where $s_F = S_F/N$ has the form shown below,

$$s_F(N,T,V) = \ln\left[\left(\frac{mk_BT}{h^2/2\pi}\right)^{\frac{3}{2}}\left(\frac{V}{N}\right)\right] + \frac{5}{2} \quad (23)$$

and consequently,

$$\frac{\partial s_F}{\partial N} = -\frac{1}{N} \quad (24)$$

By inspection, comparing Equation (22) with Equation (20) for the case $\partial s/\partial N<0$ [shown in Equation (24)] clearly

$$c = 1 \quad (25)$$

for the ideal, monatomic gas, as expected.

Entropy Fluctuations in a Small Volume

The entropy density is defined as S/V. For a small volume *v* of an ideal gas, entropy fluctuations are related to fluctuations of pressure p and density ρ via Equation (26)[10]

$$\partial S = \frac{3v}{2T}\left(\partial p - \frac{5}{3}p\frac{\partial\rho}{\rho}\right) \quad (26)$$

Using the ideal gas law, $pv=Nk_BT$, Equation (26) reduces to Equation (24), consistent with c=1.

Equations for the entropy of other real systems, if known, are expected to similarly yield appropriate values for c.

Conclusion

The form of the stretched exponential $e^{-(kt)^c}$ is consistent with several mechanisms. For c<1, initial decay events may probabilistically decrease the rate of subsequent events or, for c>1, initial events may increase the rate of subsequent events. There may also be predetermined distributions of decay times or decay paths. For probabilistic contributions to stretched exponential behavior, the exponent c in the stretched exponential $e^{-(kt)^c}$ is related to the chemical potential μ of the system at the onset of the decay process. The physical structure of systems exhibiting stretched exponential behavior and the statistical mechanics of how these structures are populated or depopulated probably both play a role in the dynamics of these systems.

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Author Biography

Eric Stelter works on electrographic development and related technologies at NexPress Solutions Inc., where he is a Senior Scientist in the Advanced Development group. He has been granted more than 25 patents in this field. He began his career at Eastman Kodak Company after receiving his Ph.D. in physics from the University of Illinois in 1985. He is an active member of IS&T, the American Physical Society, and the American Association for the Advancement of Science.