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Comment

History of the Kohlrausch (stretched exponential) function: Pioneering work in luminescence

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Important elements for the history of the Kohlrausch (or stretched exponential) relaxation function were recently presented by Cardona, Chamberlin, and Marx [1].

The Kohlrausch function is given by

$$P(t) = \exp\left[-(t/\tau_0)^{\beta}\right] \ , \tag{1}$$

where $P(t)$ is a linear function of a property of a system that evolves towards equilibrium after the sudden removal of a perturbation, $0 < \beta \leq 1$, and τ_0 is a parameter with the dimensions of time.

In studies of the relaxation of complex systems, the Kohlrausch function is frequently used as a purely empirical relaxation function, given that it allows gauging in a simple way deviations from the "canonical" single exponential behaviour by means of the parameter β. There are nevertheless theoretical arguments to justify its relatively common occurrence.

The first use of the stretched exponential function to describe the time evolution of a non-equilibrium quantity is usually credited to Rudolph Kohlrausch (1809–1858), who in 1854 [2] applied it to the discharge of a capacitor (Leyden jar), after concluding that a simple exponential of time was inadequate [3].

Like Cardona, Chamberlin, and Marx [1], the present authors also commented on the frequently careless citation of Kohlrausch's work [4], for which about two-thirds of the citations are incorrect [1]. This is unfortunately a common situation with respect to historical papers [5].

We would like now to draw attention to a set of pioneering works on the Kohlrausch function, one of which published 101 years ago [6], and that are not mentioned in [1]. All these uncited works pertain to the description of luminescence decays, and are briefly discussed in [4] and [7] in connection with the stretched exponential relaxation function.

The Kohlrausch function was most likely used for the first time in luminescence by Werner in 1907 [6], in order to describe the short-time luminescence decay of an inorganic phosphor. This pioneering work by Werner, a Ph. D. student of Philipp Lenard [8] in Kiel, has received only 8 SCI citations, however, one of these comes from a paper by Marsden [9]. The article is also cited in a monograph (where we found it) [10], and in a few more books [11, 12]. In his article, Werner does not cite Kohlrausch, and again uses the Kohlrausch function as an empirical function. Werner's work is thus the second documented use of the Kohlrausch function.

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In the field of condensed matter luminescence, the Kohlrausch function has firm grounds on several models of luminescence quenching, namely diffusion-controlled contact quenching [13] (75 citations), where the transient term has $\beta = 1/2$, and diffusionless resonance energy transfer by the dipole-dipole mechanism, with $\beta = 1/6$, $1/3$ and $1/2$ for one, two and three dimensions, respectively, see [14] (1139 citations) and [15] (23 citations). Other rational values of β are obtained for different multipole interactions, e.g., $\beta = 3/8$ and $\beta = 3/10$ for the dipole-quadrupole and quadrupole-quadrupole mechanisms in three-dimensions [16] (1099 citations).

All these works [6, 13–16] antedate (in the Werner case by many decades) the 1970 Williams and Watts paper on dielectric relaxation, and are a significant part of the history of the stretched exponential relaxation function.

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