Analysis of signals from superposed relaxation processes

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System functions of many linear physical systems or autocorrelation functions of their output signals are often a sum of relaxator terms with different relaxation times and amplitudes. In the time domain a superposition of exponential decays $e^{-\gamma t}$ is observed, while in the frequency domain a sum of relaxator terms of structure $1/(\gamma + i\omega)$ is measured. Thus, the response is either the Laplace transform of the system function or its Stieltjes transform, respectively. In both cases it is the task of an analyst to gain the relaxation times and weights from the measured signal. An exact reconstruction of the system function is limited by the noise, measuring time, and number of points measured. In this paper procedures for the approximate reconstruction of the system function are introduced. The equivalence of most of them is shown and their properties are discussed. An expression for the limit of resolution is derived for a given signal-to-noise ratio. The results are applicable to experimental data from various physical systems. For illustration the autocorrelation function of the light scattered from polymer solutions and the response of photoconductors are used.

I. INTRODUCTION

For numerous examples of linear physical systems, the system function can be represented by a superposition of relaxator terms (with relaxation frequency γ). Thus in the time domain the system function $f(t)$ can be written as

$$f(t) = \int_0^\infty e^{-\gamma t} g(\gamma) d\gamma, \quad t \geqslant 0, \tag{1}$$

or, if the distribution is of discrete form $g(\gamma) = \Sigma_n a_n \delta(\gamma - \gamma_n)$,

$$f(t) = \sum_n a_n e^{-\gamma_n t}. \tag{2}$$

The physical system is then completely described by the distribution function $g(\gamma)$ in Eq. (1); cf. the set $\{a_n\}$ in Eq. (2).

In the frequency domain, the system function is given by

$$f(\omega) = \int_0^{+\infty} \frac{1}{\gamma + i\omega} g(\gamma) d\gamma, \tag{3}$$

or an equivalent sum, if the distribution is of discrete form. The problem to be solved is the inversion of Eqs. (1) and (3) for $g(\gamma)$; cf. Eq. (2) for the set $\{a_n\}$.

Equations (1)–(3) are examples of Fredholm integral equations of the first kind, with a kernel function which depends only on the product of the introduced variables (γt; cf. ω/γ). Actually, the inversion of nearly all integral equations of the first kind represents an ill-posed problem, and a solution has to overcome this difficulty.

For practical purposes it is important to know in which way a method applied overcomes the ill-posedness of the inversion problem. But it is of the same importance to know the limits of a method, to be able to determine if it produces relevant results or rubbish. We do not treat the problem in a formal mathematical way, but we want to generate evident pictures, which are helpful for the practical use.

The paper is organized as follows: In Sec. II the nature of the ill-posedness of the inversion problems Eqs. (1)–(3) is illustrated by a simple argument. In Sec. III several proposals for the inversion of Eq. (1) are given in detail: the application of the well-known inversion formula for the Laplace transform,[1] the twofold mapping method, developed by Dohler and Gotze[2] and Link,[3] the differential operator method, developed by Love and Byrne[4] and Lustig,[5] the eigenfunction expansion of McWhirter and Pike,[6] and the deconvolution method, introduced by Gardner, Gardner, and Meinke.[7] In Sec. IV it is shown that the proposals of Refs. 4–7 can be mapped onto each other. In Sec. V a simple estimate for the resolution of the inversion procedures is derived. In Sec. VI it is shown that methods for an approximate solution of the inversion problem can be constructed and visualized by using a filter concept.[8] Section VII gives a short description for the deconvolution in the frequency domain. Section VIII shows the practical questions of inversion procedures by two different kinds of experiments, quasi-elastic light scattering[3,9] and response of photoconductors.[10,11] Recently introduced other physical applications include MEDLTS (multiexponential deep-level transient spectroscopy),[12,13] photoacoustic depth profiling,[14] and the thermal wave analysis of pyroelectricity distributions[15,16] in polymeric films. The results may also be applied to other problems in physics, as, for example, the inversion of the moment expansion,[17] which is equivalent to a Laplace transform known on a discrete set of points. An application of this inversion problem can be found in QCD.[18]

II. INFLUENCE OF NOISE

Ill-posedness is a feature of virtually all inversion problems associated with integral equations of the first kind. The ill-conditioned nature of the inversion of Eq. (1) can be illustrated in a very simple manner. Let us consider the effect of some arbitrary oscillating term $a_\omega \sin(\omega\gamma)$ added to the so-

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