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Relaxation Dynamics of Cascaded Linear Processes

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In many fields of nature, a system reacts to sudden changes of an external parameter in the form of two (or more) cascaded relaxation processes, where the first step depends directly on the external parameter and the second process, which is connected with the experimental observable, is determined by the state of relaxation of the first one. It follows from linear-response theory that in this case the experiment yields a behavior which distinctly deviates from a single-exponential decay, even if each of the processes is linear and follows an exponential law. The relaxation starts with time derivative zero, which is most pronounced when the two time constants are of similar magnitude. If the experimental data are fitted with a Kohlrausch−Williams−Watts (KWW) function, the fit will therefore tend to overestimate the KWW exponent β. Even β values larger than one can be obtained. As an example, the diffracted light signal in a photorefractive polymer is analyzed.

In nature, relaxation processes are often cascaded. This means that a system contains (at least) two dynamical processes, one of which reacts directly to an external parameter, whereas the second one, which is observed or connected with an observable quantity, depends on the first process. Prominent examples occur in the fields of photorefractive polymers[1] and thermodiffusion in a liquid (the Ludwig−Soret effect).[2]

Photorefractive polymers consist of a matrix of low glass transition temperature (around or below room temperature) and contain photoconductive moieties and highly anisotropic chromophores (often with nonlinear-optical properties). By irradiating crossed laser beams, a light intensity grating is formed, which gives rise to charge separation in the bright areas and, as a consequence, to the formation of a space charge grating. Together with a strong homogeneous external electric field, this leads to a modulated alignment of the chromophores[3] and a refractive-index grating (or phase hologram), which is shifted with respect to the light intensity grating.[4] The amplitude of the phase hologram is usually measured by its diffraction efficiency using a third laser beam. When the external field or one of the writing beams is turned on or off, the space charge distribution is directly affected and relaxes toward its new equilibrium. This, in turn, leads to a relaxation of the chromophore alignment, which is observed as a change of the diffraction efficiency.

Thermodiffusion is a material transport in solutions or mixtures of liquids driven by a temperature gradient $\nabla\Theta$. The concentration c of a species in the mixture changes with time according to

$$\frac{\partial c}{\partial t} = D\Delta c + D_\Theta \nabla[c(1-c)\nabla\Theta] \qquad (1)$$

where D is the mass and D_Θ is the thermal diffusion coefficient. An elegant experiment for investigating this effect uses again a light intensity grating, which gives rise to a temperature grating in the liquid.[5] The concentration grating created by the Ludwig−Soret effect is probed by its diffraction efficiency. Also in this case the measured quantity (the concentration grating) reacts only indirectly (via the temperature grating) to changes of the external parameter (the light intensity grating).

In this paper, we investigate the general relaxation behavior of the secondary process, which is related to the experimental observable, upon a sudden change of the external parameter. We assume that the whole system is linear; that is, the response of each single process depends linearly on the amplitude of the excitation. First we consider a switching-on process at $t = 0$, so we can analyze the problem in terms of linear-response theory.

To this end, we introduce the linear-response functions $g_1(t)$ and $g_2(t)$ for processes 1 and 2, respectively; they are defined as the answer of the processes to a pulse excitation. Then the measured signal $I(t)$, which is the response of the whole system to an arbitrary excitation $x(t)$, can be expressed as

$$I(t) = g_2(t) \otimes [g_1(t) \otimes x(t)] = [g_2(t) \otimes g_1(t)] \otimes x(t) = g(t) \otimes x(t) \qquad (2)$$

where $\otimes$ denotes temporal convolution. The behavior of the combined processes is described by a single linear-response function

$$g(t) = g_2(t) \otimes g_1(t) = \int_{-\infty}^{t} g_2(t-\tau)\, g_1(\tau)\, \mathrm{d}\tau \qquad (3)$$

In the special case of exponential response functions

$$g_k(t) = \left\{ \begin{array}{ll} (A_k/T_k)\exp(-t/T_k) & \text{for t} \geq 0 \\ 0 & \text{for } t < 0 \end{array} \right\} k = 1 \text{ and } 2 \qquad (4)$$

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it reads

$$g(t) = \frac{A_1A_2}{T_2 - T_1}\left[\exp\left(-\frac{t}{T_2}\right) - \exp\left(-\frac{t}{T_1}\right)\right] \quad \text{for } T_1 \neq T_2 \tag{5}$$

and

$$g(t) = \frac{A_1A_2}{T^2}t\exp\left(-\frac{t}{T}\right) \quad \text{for } T = T_1 = T_2 \tag{6}$$

Since the linear-response function as given in eqs 5 and 6 describes the answer of the combined system to a pulse excitation, it is also of great practical importance, e.g., for the evaluation of fluorescence lifetime measurements. Here T_1 is the fluorescence lifetime to be determined and T_2 the time constant of the detection apparatus.

The time-dependent susceptibility $\chi(t)$ is defined as the system response to a step excitation of amplitude unity starting at $t = 0$

$$\chi(t) = \int_0^t g(t - \tau)\,\mathrm{d}\tau = \int_0^t g(\tau')\,\mathrm{d}\tau' \tag{7}$$

With eqs 5 and 6, the integral yields

$$\chi(t) = \frac{A_1A_2}{T_2 - T_1}\left\{T_2\left[1 - \exp\left(-\frac{t}{T_2}\right)\right] - T_1\left[1 - \exp\left(-\frac{t}{T_1}\right)\right]\right\} \quad \text{for } T_1 \neq T_2 \tag{8}$$

and

$$\chi(t) = A_1A_2\left[1 - \left(1 + \frac{t}{T}\right)\exp\left(-\frac{t}{T}\right)\right] \quad \text{for } T = T_1 = T_2 \tag{9}$$

respectively.

Finally, the dynamical (or frequency-dependent) susceptibility $\chi^*(\omega)$ is measured in an experiment with oscillatory excitation $x(t) = x_0 \exp(-i\omega t)$ and the corresponding signal $I(t) = I_0^*(\omega) \exp(-i\omega t)$. It is related to the complex signal amplitude $I_0^*(\omega)$ and is the Fourier transform of the linear-response function

$$\frac{I_0^*(\omega)}{x_0} = \chi^*(\omega) = \chi'(\omega) - i\chi''(\omega) = \int_{-\infty}^{+\infty} g(t)\exp(-i\omega t)\,\mathrm{d}t \tag{10}$$

According to the convolution theorem, the Fourier transform of $g(t) = g_2(t) \otimes g_1(t)$ for the cascaded processes is the product of the Fourier transforms of $g_1(t)$ and $g_2(t)$

$$\chi^*(\omega) = \frac{A_1}{1 + i\omega T_1}\frac{A_2}{1 + i\omega T_2} \tag{11}$$

that is, it is the product of two Lorentzians. The fact that the product of two Lorentzians is *not* Lorentzian, but falls off more rapidly for $\omega \rightarrow \pm\infty$, corresponds to the deviation from a single-exponential temporal decay.

The response of two cascaded relaxation processes to a switching-off process is closely related to the time-dependent susceptibility. In this case the signal of the combined system is simply given by

$$I(t) = \chi(\infty) - \chi(t) \tag{12}$$

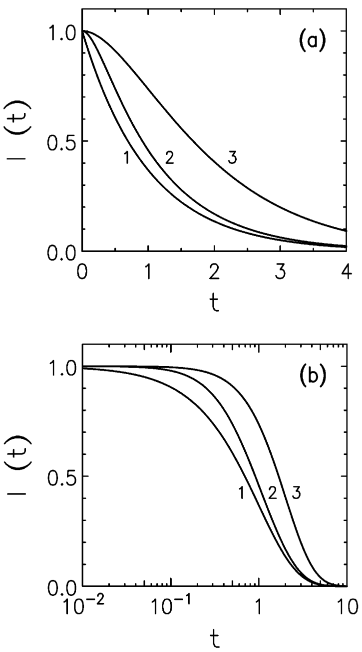

Figure 1. Relaxation of two cascaded processes on a linear (a) and a logarithmic (b) time scale. Curve 2 corresponds to eq 13 with $T_2 = 1$ and $T_1 = 0.2$, curve 3 to eq 14 with $T = 1$ ($A_1A_2 = 1$). Curve 1 shows an exponential function with relaxation time 1 for comparison.

If both processes are single-exponential, it reads

$$I(t) = \frac{A_1A_2}{T_2 - T_1}\left[T_2\exp\left(-\frac{t}{T_2}\right) - T_1\exp\left(-\frac{t}{T_1}\right)\right] \quad \text{for } T_1 \neq T_2 \tag{13}$$

and

$$I(t) = A_1A_2\left(1 + \frac{t}{T}\right)\exp\left(-\frac{t}{T}\right) \text{ for } T = T_1 = T_2 \tag{14}$$

Equations 8, 9, 13, and 14 describe a behavior which is distinctly different from a single-exponential decay, since for $t \rightarrow 0$ the time derivative of $I(t)$ is zero. This feature is particularly pronounced when the relaxation times T_1 and T_2 are of comparable magnitude (see Figure 1). Only for $T_1 \ll T_2$ and $T_1 \gg T_2$ single-exponential laws are approached, but even when T_1 and T_2 differ by a factor of 5, the relaxation is clearly non-single-exponential. This behavior of two cascaded linear systems is not intuitively obvious. It has unexpected consequences for the evaluation of experimental data. If the decay curve is fitted with an exponential, there are deviations at short times and, moreover, the obtained time constant is too long, as is most clearly seen from eq 14 and Figure 1. Even more unexpected results are obtained from fits with a stretched-exponential (or Kohlrausch−Williams−Watts [KWW]) function

$$I_{\mathrm{fit}}(t) = I_0\exp\left[-\left(\frac{t}{T}\right)^{\beta}\right] \tag{15}$$

The exponent β is usually between 0 and 1. $\beta = 1$ corresponds to one single relaxation time (T), whereas for $\beta < 1$ a distribution of relaxation times (or relaxation rates) is present, whose width increases with decreasing β. In the case of $\beta < 1$, the derivative of a stretched exponential tends to infinity for $t \rightarrow 0$. This is in striking contrast to the behavior of eqs 13 and 14. A fit with a stretched exponential therefore yields an exponent β *above* one (and again, in general, an incorrect time constant T). $\beta > 1$ cannot be interpreted in terms of a physically

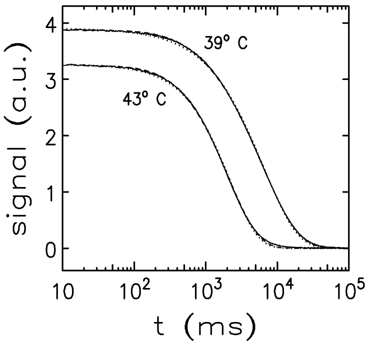

Figure 2. Diffracted light signal in a photorefractive polymer after turning off one of the writing beams. Solid lines, experimental data; dashed lines, fit with the model described in this paper; dotted lines, fit with a stretched-exponential function. For the parameters of the functions see text.

meaningful distribution of relaxation times. It is a direct consequence of the fact that one of the exponentials in eq 13 has a negative sign.

The above model, which assumes both $g_1(t)$ and $g_2(t)$ to be single exponentials, is often too simple for real systems. A more realistic description is to choose one of the functions as single-exponential and the other one in such a form that it comprises a distribution of relaxation times (e.g., the derivative of a KWW law). For instance, in photorefractive polymers, the decay of the space charge field usually follows a single-exponential law, whereas the reorientation dynamics can be described by a stretched exponential.[6,7] Alternatively, a power-law time dependence was proposed for the reorientation, which corresponds to a temporal decrease of the rotational diffusion coefficient of the chromophores as $D(t) = D_0/t$.[8,9] A general analytical solution of the integrals in eqs 3 and 7 is not possible in this case. We can, however, express the complicated function (say, g_2) by its inverse Laplace transform and perform the calculation for each of its exponential components. The result reads

$$I(t) = A_1 A_2 \int_0^\infty \frac{F_2(1/T_2)}{T_2 - T_1}\left[T_2 \exp\left(-\frac{t}{T_2}\right) - T_1 \exp\left(-\frac{t}{T_1}\right)\right] \mathrm{d}(1/T_2) \quad (16)$$

$F_2(1/T_2)$ is the rate distribution function of $g_2(t)$. Also this expression has exponential contributions with negative sign. Hence, a KWW fit will again tend to yield too large a β value, in particular, when T_1 falls within the range of the T_2 distribution. For a detailed analysis of experimental data, the integral in eq 16 must be calculated numerically.

We demonstrate our model with the decay of the holographic grating in a photorefractive polymer.[7] The solid lines in Figure 2 represent the diffracted light signal as a function of time after blocking one of the hologram writing beams. The experiment was performed at two different temperatures. The amplitude of the holographic grating was described with our model discussed above (dashed lines) and, alternatively, with a simple KWW function with time constant T (dotted curves). Within our model, we assumed that the first process (the decay of the space charge field) follows an exponential law, whereas the second step (the chromophore reorientation) is given by a KWW function. The grating amplitude could, in principle, be calculated from eq 16, but since there is no simple analytical formula for the decay rate distribution $F_2(1/T_2)$ of a KWW function, a numerical convolution procedure similar to eqs 3−12 was performed. For $g_1(t)$ an exponential as in eq 4 and for $g_2(t)$ the derivative of a KWW function with time constant T_2 was inserted. We took into account that the diffracted light signal is proportional to the square of $I(t)$.

The fit of the data at 43 °C with our model yields a KWW exponent $\beta = 1$ within the experimental uncertainty. Hence, we kept $\beta = 1$ fixed and fitted only the time constants T_1 and T_2 (and the prefactor). The results are $T_1 = 140$ ms and $T_2 = 4.10$ s, respectively. The fit with the simple KWW function gives $T = 4.07$ s and $\beta = 1.13$. For the data at 39 °C, our model yields $T_1 = 180$ ms, $T_2 = 13.98$ s, and $\beta = 0.87$, whereas the KWW fit results in $T = 13.70$ s and $\beta = 0.92$.

The dashed curves represent the experimental data very well. Also the KWW fits (dotted curves) are quite satisfactory. In the latter case, however, the KWW exponent β is larger at both temperatures and even exceeds 1 at 43 °C. This unphysical result does not occur with the cascaded-step model. The time constants of the KWW function, on the other hand, are very similar in the two models. This is due to the fact that the decay time of the space charge field (T_1) is shorter by at least 1.5 orders of magnitude, and hence, the two processes are largely decoupled. The glass transition temperature of the photorefractive polymer is 36 °C. Thus, it is reasonable that the reorientation dynamics at 43 °C is well described by a single-exponential law, whereas it consists of a distribution of relaxation rates (corresponding to $\beta < 1$) at 39 °C, which is only 3° above the glass point.

For both fit functions, the residuals are roughly one percent of the signal amplitude. Our model yields a slightly better fit than the KWW function; this, however, can be due to the fact that one more free parameter is used. Residuals on the order of one percent are quite acceptable and may be due to slight detector nonlinearities or instabilities of the experimental setup. The important result is that the fit with our model yields KWW exponents $\beta \leq 1$.

In summary, we have investigated the functional form of the relaxation dynamics of two cascaded linear processes. Specifically, we have calculated the experimental response function for a steplike perturbation, when the first process reacts directly to the external perturbation and the observable depends on the second process which, in turn, reacts to the first one. The nonintuitive result is that even in the simplest case, when both processes follow exponential functions, the relaxation differs from a single-exponential decay, starting with time derivative zero. This behavior is most strongly pronounced when the two relaxation times are of similar magnitude. Analyzing the experimental relaxation curve with a stretched exponential then yields an exponent $\beta > 1$ and an incorrect time constant T. The problem was analyzed within the formal framework of linear-response theory. It was shown that the experimental signal is given by the time-dependent susceptibility of the cascaded processes and that its deviation from a single-exponential form is also reflected by the dynamical susceptibility. The model was used to evaluate the decay of the diffracted light intensity in a photorefractive polymer after turning off one of the writing beams.

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