Delay-Controlled Reactions

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Abstract

When the entities undergoing a chemical reaction are not available simultaneously, the classical rate equation of a reaction or, alternatively for the evolution of a population, should be extended by including non-Markovian memory effects. We consider the two cases of an external feedback, realized by fixed functions and an internal feedback originated in a self-organized manner by the relevant concentration itself. Whereas in the first case the fixed points are not changed, although the dynamical process is altered, the second case offers a complete new behaviour, characterized by the existence of a time persistent solution. Due to the feedback the reaction may lead to a finite concentration in the stationary limit even in case of a single-species pair annihilation \( A + A \rightarrow 0 \) process. We argue that the different cases are similar to a coupling of additive or multiplicative noises in stochastic processes.

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I. INTRODUCTION

Chemical reactions involving different species are described by classical rate equations in which the time evolution for the forward and reverse reactions are balanced by the product of the concentration of the reacting entities, see for a recent review [1]. The approach is based on the assumption that the reactants are available simultaneously. In the one species-annihilation process a particle $A$ is annihilated upon encounter according to the reaction scheme $A + A \rightarrow 0$. The reaction is immediate and is realized with a certain rate $\nu$. During the related one-species coalescence process $A + A \rightarrow A$ the reactants fuse together realized with another rate $\mu$. The time evolution of the global concentration $c(t)$ obeys the mean field equation

$$\frac{dc(t)}{dt} = -(2\nu - \mu)c^2$$

whereas $\nu$ and $\mu$ are the coalescence and annihilation rates. In case the reaction takes place only after a sufficient accumulation of the reactants, the reaction process is changed crucially. We demonstrate that the long-time behaviour is typically dominated by such delay effects. The system is able to reach a stationary state instead of exhibiting an algebraic decay in time as it follows using Eq. (1). Let us illustrate the situation in mind in more detail. Generally the time evolution of the concentration $c(t)$ is characterized by gain and loss terms. Moreover, the concentration could also depend on the history of the sample to which it belongs. In the same sense the changing rate of the concentration should be influenced by the changing rate in the past. Thus the evolution for $c(t)$ has to be supplemented by a memory term indicating the non-Markovian behaviour. Such a term models, for instance the way on which a seed concentration had been accumulated by a delayed transport mechanism originated by the environment of the reactants. With other words, the changing rate of a certain quantity at time $t$ is also determined by the accumulation rate at a former time $t' < t$. In between, i.e. within the interval $\tau = t - t'$, the reactants are enriched while changing the concentration at $t'$. Regardless that process and further fluctuations the available amount of concentration at time $t$ is governed by instantaneous gain and loss of concentration as well as on the changing rate at former times $t'$. Consequently the evolution Eq. (1) should be modified according to

$$\partial_t c(t) = rc(t) - uc^2(t) - \int_0^t K(t, t'; c) \partial_{t'} c(t') dt'$$

(2)
The last term represents a permanent re-evaluation of the reactions. Hence the aim of the present paper is to study models which follow an evolution equation as given by Eq. (2) where the memory kernel $K$ will be specified below. As a new ingredient we assume that the memory term may depend on the concentration $c(t)$ and its derivative as already indicated in Eq. (2). Whereas the first realization consists of a kernel, given by a deterministic function, the second case is characterized by a kernel, determined by the concentration itself. The first case is denoted as an external feedback with a distributed time-delay, the second one is signified as an internal delay, since the time scale of the kernel is defined in a self-organized manner by the time scale of the concentration itself.

Our model can be grouped into the increasing interest of incorporating delay and feedback mechanism in a large variety of systems. Obviously the crucial factor governing the dynamics of systems comprising many "units" consists of interaction and competition. Such features are believed to underlie the complex dynamics observed in disciplines as diverse as economics, biology and weather, politics, medical care, and ecology. As discussed recently and also stressed by the present paper another characteristic trait of physical as well as biological systems is played by the mentioned time-delayed couplings. Such memory effects, considered in a large variety of systems, could be a further unifying feature of complex systems. It is well-known that evolution equations with memory kernels as it is presented by Eq. (2), can be derived following the well established projector formalism due to, see also. That approach had been applied successfully for the density-density correlation function in studying the processes in undercooled liquids. Recently a Fokker-Planck equation with a non-linear memory term was used to discuss anomalous diffusion in disordered systems. The results could be confirmed by numerical simulations including diffusion on fractals, see also. Moreover, it had been demonstrated that mobile particles remain localized due to the feedback-coupling. Notice that a formal solution of whole class of non-Markovian Fokker-Planck equations can be expressed through the solution of the Markovian equation with the same Fokker-Planck operator. The non-Gaussian fluctuations of the asset price can be also traced back to memory effects. An additional cumulative feedback coupling within the Lotka-Volterra model, which may stem from mutations of the species or a climate change, leads to a complete different behaviour compared to the conventional model. If the Ginzburg-Landau model for the time evolution of an order parameter is supplemented by a competing memory term, the
asymptotic behaviour and the phase diagram is completely dominated by such a term \[22\]. Different to our self organized approach with \( K(t, t'; c) \) there is a broad class of models with delay integrals without a dependence on the variable \( c(t) \) \[23, 24, 25\], for a survey and applications in biology see \[26\]. The spreading of an agent in a medium with long-time memory, which can model epidemics, is studied in \[27\]. Time-delayed feedback control is an efficient method for stabilizing unstable periodic orbits of chaotic systems \[28\]. It may also induce various patterns including travelling rolls, spirals and other patterns \[29\]. A further approach concerns the study of bistable time-delayed feedback systems driven by noise \[30\]. Based on a former paper \[31\] the distribution function of the first-passage-time is analysed where both, the delay and the noise term offers a significant influence on the behaviour. A global feedback is studied recently also in a bistable system \[32\]. The purpose of that paper is a discussion of the domain-size control by a feedback. Even in an open quantum system non-Markovian dynamics is characterized by a time-non-locality in the equation of motion for the reduced density operator \[33\].

In view of the large variety of systems with feedback couplings it seems to be worth to study simple models, which still conserve the crucial dynamical features of evolution models as non-linearities and moreover as a new ingredient, delayed feedback-coupling. In the present paper we demonstrate the crucial influence of the non-Markovian memory term on chemical reactions, where the retardation effects are comprised into a memory kernel \( K(t) \). That memory kernel yields an additional competitive term to the instantaneous non-linear terms.

II. EXTERNAL FEEDBACK

A. Discrete time-delay

In this section we specify the model, Eq. \[2\], by fixing the memory kernel \( K \) in terms of deterministic functions. This procedure is well-known in the framework of population dynamics (an introduction is given in \[34\]). Different to these approach our rate equation \[2\] offers a feedback-coupling to the decay rate of the population or the density of a chemical species \( \partial_t c(t) \), respectively. By choosing the kernel \( K(t, t'; \tau) = \mu \delta(t - t' - \tau) \), and substituting \( K \) in the dimensionless form of Eq. \[2\], one gets a discrete time-delayed differential
equation

$$\frac{dc(t)}{dt} = c(t) - c^2(t) - \mu \frac{dc(t - \tau)}{dt}.$$ \hspace{1cm} (3)

Here the quantity $\tau$ is the delay time which is assumed to be short ranged $\tau \ll t$. If $\tau = 0$, it results in a modification of the evolution equation for the logistic growth, which is solvable (see below). The limiting case $\tau \to 0$ can be obtained by expanding the delayed term of Eq. (3). This leads to an equation

$$\frac{d^2c}{dt^2} - \frac{1 + \mu}{\mu \tau} \frac{dc}{dt} + \frac{1}{\mu \tau} c[1 - c] = 0 \hspace{1cm} \mu \neq 0,$$ \hspace{1cm} (4)

which cannot be solved in closed form due to the non-linearity. One gets an analytical solution, if one neglects the non-linearity, which corresponds to the exponential growth of the particle density in addition of a feedback-coupling. Using standard methods the solution $c(t)$ is given by

$$c(t) = C_1 \exp(\kappa_+ t) + C_2 \exp(\kappa_- t) \hspace{1cm} \text{with} \hspace{1cm} \kappa_\pm = \frac{1}{2 \mu \tau} \left(1 + \mu \pm \sqrt{(1 + \mu)^2 - 4 \mu \tau}\right).$$ \hspace{1cm} (5)

The integration constants can be calculated to $C_1 = c_0 \frac{\kappa_+ - 1}{\kappa_- - \kappa_+}$ and $C_2 = c_0 \frac{1 - \kappa_-}{\kappa_- - \kappa_+}$, if one suggests $c(0) = c_0$ and $\frac{dc}{dt} = c_0$. Discussing the stability of Eq. (5) one finds out, that for $\mu > 0$ the both exponents $\kappa_\pm$ are positive. In case of $\mu < 0$ one of them is positive, i. e. there are no bounded solution in the limit $t \to \infty$. Alternatively, one can treat the differential equation with delay by using the Laplace transformation. Denoting the transformed function by $c(z) \equiv \mathcal{L}\{c(t)\} = \int_0^\infty c(t) \exp(-zt)dt$ the transformed function of the linear equivalent of Eq. (3) obeys the relation

$$c(z) = \frac{c_0 [1 + (1 + \mu) \exp(-\tau z)] - c(-\tau) + z \exp(-\tau z) \int_0^\infty \exp(-\tau \xi) c(\xi) d\xi}{z [1 + \mu \exp(-\tau z)] - 1}.$$ \hspace{1cm} (6)

As displayed by the last relation, differential equations with delayed terms are distinguished from conventional equations by one important feature, that the function $c(t)$ has to be given within the whole interval $-\tau < t < 0$ and not only at one special point $c(t = 0) = c_0$. Fixing $c(t) = c_0$ in that interval $-\tau < t < 0$, then the Eq. (6) becomes simpler

$$c(z) = \frac{c_0}{z - \frac{1}{1 + \mu \exp(-\tau z)}}.$$ \hspace{1cm} (7)

This equation has to be transformed back. Since the zeros of the denominator of Eq. (7) are not available analytically, the function $c(t)$ could not be not calculated exactly. However,
one can convince that in the long time limit, $z \tau \ll 1$, the concentration $c(t)$ offers an exponential form, already obtained in Eq. (5).

**B. Distributed time-delay - Exponential kernel**

An usual choice of a kernel in problems dealing with continuously distributed time-delay is the exponential kernel $K(t, t') = \mu \exp[-\lambda (t - t')]$ ($\lambda > 0$), which satisfies some properties like the boundedness and positivity of the kernel. The parameter $\lambda$ determines the time scale of the memory. Substituting this kernel in dimensionless form of Eq. (2) it leads to the following equation

$$
\partial_t c(t) = c(t) - c^2(t) - \mu \int_0^t \exp[-\lambda (t - t')] \partial_{t'} c(t') \, dt' \quad c(0) = c_0 .
$$

(8)

Fixed points of this equation are $c_s = 0$ and $c_s = 1$. They are independent of the memory parameter $\mu$ which is a general result, compare the discussion at the end of this section. To gain information about their stability, we investigate the linear equation in analogy to Eq. (8) firstly. Using Laplace transformation results in

$$
c(z) = c_0 \frac{z + \lambda + \mu}{(z - 1)(z + \lambda) + \mu z} .
$$

(9)

The zeros of the denominator of the latter formula are given by $z_\pm = 1/2 \pm \sqrt{D}$ with $D = (\lambda + \mu - 1)^2 + 4 \lambda$. It is obvious that $D > 0$, because the assumption $\lambda > 0$. Further one observes that $\sqrt{D} > |\lambda + \mu - 1|$ and so $z_+$ is positive and $z_-$ is negative. Because the structure of the solution is $c(t) = A \exp(z_+ t) + B \exp(z_- t)$, we found only unstable or unbounded solutions (for $t \to \infty$), respectively. That means that the exponential growth, which is observed in case of $\mu = 0$, could not be restricted through the additional feedback term. Alternatively, Eq. (8) can be analysed by a repeated differentiating with respect to $t$ and a renewed use of the first order equation to eliminate the integral. The procedure results in the second order equation

$$
\frac{d^2 c}{dt^2} + [2 c + \lambda + \mu - 1] \frac{dc}{dt} + \lambda c [c - 1] = 0 \quad \text{with} \quad c(0) = c_0 \quad \text{and} \quad \frac{dc(0)}{dt} = c_0 [1 - c_0] .
$$

(10)

that linear equivalent exhibits the same behaviour found above. The non-linear Eq. (10) gives rise to a more complex stability behaviour. To get insight into the stability behaviour
of both fixed points we take the ansatz \( c(t) = c_s + \varphi(t) \). Substituting this ansatz into Eq. (8) and omitting all terms of order \( \varphi^2 \) one gets the equations for \( \varphi(t) \)

\[
\dot{\varphi}(t) = \pm \varphi(t) - \mu \int_0^t \exp[\lambda(t-t')] \dot{\varphi}(t') \, dt',
\]

where the positive sign corresponds to \( c_s = 0 \) and the negative one to \( c_s = 1 \). The equation for the positive sign is already discussed above, and it follows that the trivial solution \( c_s = 0 \) is an unstable fixed point. To gain the stability behaviour of the second fixed point we follow the same steps as above. The Laplace transform of \( \varphi(t) \) is denoted as

\[
\varphi(z) = L\{\varphi(t)\}(z) = \int_0^\infty \varphi(t) \exp(-zt) \, dt.
\]

We get

\[
\varphi(z) = \varphi_0 \frac{z + \lambda + \mu}{(z + 1)(z + \lambda) + \mu z}.
\]

In this case the zeros of the denominator are given by 

\[1/2 \, \left[-(1 + \lambda + \mu) \pm \sqrt{D}\right],\]

where the discriminate is \( D = (1 + \lambda + \mu)^2 - 4 \lambda \). The solution of \( \varphi(t) \) (for \( D \neq 0 \)) can be written as

\[
\varphi(t) = \varphi_0 \left[ A \exp(z_+ t) + B \exp(z_- t) \right]
\]

with the coefficients

\[
A = \frac{-1 + \lambda + \mu + \sqrt{D}}{2 \sqrt{D}} \quad \text{and} \quad B = \frac{1 - (\lambda + \mu) + \sqrt{D}}{2 \sqrt{D}}.
\]

The last formula implies that for \( D \geq 0 \) the solution is real and hence physically relevant. The limiting case \( D = 0 \) delivers critical values either for \( \mu \) or for \( \lambda \). Choosing \( \mu = \mu(\lambda) \) the critical values for \( \mu \) are \( \mu^\pm(\lambda) = -(\lambda + 1) \pm 2 \sqrt{\lambda} \). If \( \mu \) is situated in the intervals \( \mu > \mu^+ \) or \( \mu < \mu^- \), \( D > 0 \) is fulfilled and the resulting solution is real. The solution for \( \varphi \) is only stable, if \( \mu > -(1 + \lambda) \). All together the parameter \( \mu \) has to fulfil \( \mu > \mu^+ \) to get stable, physically relevant solutions. In the limiting case, \( \mu = \mu^- \), one specifies

\[
\varphi(t) = \varphi_0 \exp\left(-\sqrt{\lambda} t\right) \left[ 1 + (\sqrt{\lambda} - 1) t \right],
\]

which is a bounded solution for \( t \to \infty \). In case of \( \lambda < 1 \), \( \varphi(t) \) changes its sign at \( t^* = (1 - \sqrt{\lambda})^{-1} \). Together we can determine the stability domain for the fixed point \( c_s = 1 \) to the area in the \( (\lambda, \mu) \)-plane, where \( \mu \geq \mu^+(\lambda) \) is fulfilled. Eq. (10) is an evolution equation, which is well-known as equation for a damped oscillator. Interpreting the equation as an equation of motion for a particle in a potential \( U(c) = -c^2/2 + c^3/3 \), then the factor in front of the first derivative has the meaning of the damping constant. Due to the non-linearity of the underlying evolution equation the damping parameter \( \gamma(c) = 2c(t) + \lambda + \mu - 1 \) is
driven by the time dependent concentration. If one recognizes that only a positive damping parameter \( \gamma(c) \geq 0 \) is reasonable, it is obvious that the stability criteria is additionally depended on the initial value \( c_0 \). That is indeed a feature of systems including feedback or memory effects. With the following constraints

\[
\begin{align*}
\mu + \lambda + 1 - 2 \sqrt{\lambda} & \geq 0 \\
2 c_0 + \mu + \lambda - 1 & \geq 0
\end{align*}
\] (15)

one gets the stability domain depicted in Fig. 11 where the \((\mu, \lambda, c_0)\)-plane is displayed. The area, limited by the curved area and the plane area at the forefront, is the region where the solution is supposed to be stable.

C. Distributed time-delay - a periodic kernel

Since the dynamical behaviour is affected by the sign of the memory parameter \( \mu \), we consider now a periodic kernel such as \( K(t, t') = \mu \cos [\lambda (t - t')] \), which results in

\[
\partial_t c(t) = c(t) - c^2(t) - \mu \int_0^t \cos [\lambda (t - t')] \partial_{t'} c(t') dt' .
\] (16)

Again the two stationary values are determined to \( c_s = 0 \) and \( c_s = 1 \). The Laplace transform of the corresponding linear evolution equation is calculated to

\[
c(z) = c_0 \frac{z^2 + \lambda^2 + \mu z}{(z - 1)(z^2 + \lambda^2) + \mu z^2} .
\] (17)

The denominator is a cubic polynomial and the zeros could be calculated. At least one of the three solutions has a positive real part in case of \( \lambda \neq 0 \) and so there are only unbounded solutions for the linear equivalent of Eq. (16) for long times. Like in the case of the exponential kernel Eq. (16) can be written as a conventional differential equation which is in the present case third order

\[
\frac{d^3 c}{dt^3} + [2 c + \mu - 1] \frac{d^2 c}{dt^2} + \left[ 2 \frac{dc}{dt} + \lambda^2 \right] \frac{dc}{dt} + \lambda^2 c (c - 1) = 0
\] (18)

with the initial value \( c(0) = c_0 \), the initial slope \( \frac{dc(0)}{dt} = c_0 (1 - c_0) \) and the initial curvature \( \frac{d^2 c(0)}{dt^2} = c_0 (1 - c_0) (1 - \mu - 2 c_0) \). The invariance of the kernel against the inversion of \( \lambda \leftrightarrow -\lambda \) is maintained in Eq. (18), too. The third order differential equation is again equivalent to a
system of three first order equations. The linear form leads to the same results as discussed after Eq. (17). In Fig. 2 we show a typical example for the time evolution of the concentration. Obviously, an increasing value of the parameter \( \lambda \) leads to an overdamped behaviour.

The special case of a constant memory kernel \( K(t, t') = \mu \) can be treated exactly. Setting \( \lambda = 0 \) in Eq. (16) it results the following equation

\[
\frac{dc}{dt} = [1 - \mu] c(t) - c^2(t) + \mu c_0.
\]  

(19)

The decay of the concentration decay depends directly on the initial value \( c_0 \) making the memory apparently. Further the growth rate is modified by replacing \( 1 \rightarrow 1 - \mu \). The general solution for arbitrary \( \mu \) is deducible with the result

\[
c(t) = \frac{1 - \mu}{2} + \frac{\hat{D}}{2} \tanh \left[ \frac{1}{2} \hat{D} t + \hat{c} \right]
\]

with \( \hat{D} = \sqrt{(1 - \mu)^2 + 4 \mu c_0} \) and \( \hat{c} = \frac{1}{2} \ln \left[ \frac{\hat{D} + 2c_0 + \mu - 1}{\hat{D} - 2c_0 - \mu + 1} \right] \).

(20)

The last solution is only reasonable within the interval \( 0 < c_0 < 1 \). The special case \( \mu = 1 \) yields

\[
c(t) = \sqrt{c_0} \tanh \left[ \sqrt{c_0} t + \frac{1}{2} \ln \left( \frac{1 + \sqrt{c_0}}{1 - \sqrt{c_0}} \right) \right],
\]  

(21)

The characteristic width of the curve \( \tau_0 = 2 \hat{D}^{-1} \) is determined by the memory parameter \( \mu \) and the initial value \( c_0 \). For \( t \to \infty \) the solution, given by Eqs. (20, 21), lead to fixed points

\[
c_s(\mu) = \frac{1}{2} [1 - \mu \pm \hat{D}]
\]

different from \( c_s = 0 \) or \( c_s = 1 \), respectively. The negative branch is omitted, because \( c_s \) has to be positive. Contrary to the previous cases the stationary solution depends on the memory parameter \( \mu \). Concerning the non-trivial case, where \( \lambda \neq 0 \), the instability of \( c_s = 0 \) is maintained for all values of \( \mu \), whereas \( c_s = 1 \) is stable in the half-plane \( \mu > 0 \). In this area one gets a solution starting with an exponential decay (growth) which is followed by a damped oscillational motion toward the stationary solution \( c_s = 1 \), compare Fig. 2.

The analysis can be generalized to an arbitrary kernel \( K(t) \). Considering the Laplace transformed of Eq. (2), one concludes straightforwardly, that the fixed points remain unchanged, whenever the transformed memory kernel satisfies the relation

\[
\lim_{z \to 0} z K(z) = 0.
\]  

(22)
For a constant kernel that equation is not fulfilled and one finds the modified fixed point given above. Thus, an external non-trivial feedback-kernel behaves like an additive noise in stochastic processes. In the next section we demonstrate how that picture is altered by assuming an internal feedback. In that case the kernel is determined by concentration itself. As consequence the last relation is likewise violated and the stationary points are directly controlled by the memory. Such a situation is the feature of stochastic processes whenever a multiplicative noise is included.

III. INTERNAL FEEDBACK

In this section let us generalize the previous approach by including self-organized delay effects where, as already discussed in the introduction and in accordance with the conclusion of the last section, the kernel depends on the concentration \( c(t) \) itself. That means, the time scale of \( K(t) \) in Eq. (2) is determined by the time scale of \( c(t) \). Following this line that the delay effects are dominated by the concentration \( c(t) \) we conclude

\[
K(t, t'; c) \equiv K(c(t - t')) \quad . 
\]

The kernel is defined by the concentration in the intermediate interval \( t - t' \) which is coupled to the changing rate at the previous time \( t' \) as indicated in Eq. (2). The memory kernel characterizes the way on which a seed concentration had been accumulated. Within the time interval \( \tau = t - t' \), the concentration is further enriched, or with other words, at time \( t' \), only an incomplete reaction is realized. During the time interval \( t - t' \) the residual particles are moved to the reaction zone. As the simplest realization of Eq. (23) we chose a linear dependence on the concentration. In that case the memory term is a competitive one to the conventional quadratic term. Summarizing all contributions we will analyse the evolution equation

\[
\partial_t c(t) = rc(t) - uc^2(t) - \kappa \int_0^t c(t - t') \, \partial_{t'} c(t') \, dt' \quad . 
\]

The first term characterizes the spontaneous creation of particles (with rate \( r > 0 \)) in according to the reaction \( 0 \rightarrow A \), whereas the second one describes a two particle reaction discussed in the introduction, compare Eq. (1). Both terms leads to a stable stationary solution when they are balanced, manifested by \( r > 0, \, u > 0 \). For generality one could also discuss the case that the parameter \( r \) and \( u \) can vary and change their signs. Here,
we restrict us to positive quantities \( r \) and \( u \). The last term models the feedback with the coupling parameter \( \kappa \) which mimics the influence of the environment. The following results are strongly influenced by the sign of the memory strength \( \kappa \). In case of \( \kappa < 0 \) and \( u > 0 \) both non-linear terms are competitive ones. Let us remark that the memory kernel gives rise to a coupling of the time scales. In the vicinity of the upper limit of the integral \( t' \approx t \) the memory term reads \( c(0)\partial_t c(t) \), i.e. a momentary change at the observation time \( t \) is coupled to the value at the initial time \( t = 0 \). Therefore the very past is related to the instantaneous value of \( c(t) \). In the opposite case, at the lower limit \( t' \approx 0 \), the change of the concentration near to the initial value \( \partial_t c(t' = 0) \) is directly coupled to the instantaneous value \( c(t) \). In such a manner the memory term represents a weighted coupling of the behaviour at the initial time and the observation time. This coupling leads to another long-time behaviour. Notice that the generic behaviour, discussed below, is not changed by assuming other terms with different power laws in Eq. (24).

### A. Stationary solutions

In this section we find the stationary solutions of Eq. (24) and discuss their stability. An important case is realized by \( r > 0 \), \( u > 0 \) and arbitrary \( \kappa \). Introducing dimensionless quantities \( c \rightarrow r/uc, t \rightarrow t/r \) we end up with an equation

\[
\partial_t c(t) = c(t) - c^2(t) - \mu \int_0^t c(t-t') \partial_t c(t') dt'
\]

with \( \mu = \kappa / u \). The solution of the evolution Eq. (25) is simple when the memory kernel is zero, i.e. \( \mu = 0 \). It results

\[
c(t) = \frac{c_0 e^t}{1 + c_0 (e^t - 1)} \quad \text{with} \quad c_0 = c(t = 0)
\]

(26)

In the long time limit it results a non-trivial stationary and stable solution \( c_s(\mu = 0) = 1 \) and an unstable trivial solution \( c_s = 0 \). The inclusion of a memory term will change that behaviour drastically. To that aim let us analyse how the concentration is controlled by the feedback-coupling strength \( \mu \). The formal solution of Eq. (25) is obtained by using Laplace transformation. We get

\[
c(z) = \frac{c_0(1 + \mu c(z)) - A(z)}{z(1 + \mu c(z)) + 1}
\]

with \( A(z) = L(c^2(t))(z) \)

(27)
Remark that we discuss only the non-trivial memory controlled solution by assuming \( c_0 \neq 0 \) and \( c_0 \neq 1 \). Following the line of the previous section the long-time behaviour is obtained by making the ansatz \( c(t) = c_s + \varphi(t) \) or after Laplace transformation

\[
c(z) = \frac{c_s}{z} + \varphi(z)
\]

(28)

where the function \( \varphi(z) \) remains regular for \( z \to 0 \). This function will be discussed in the next subsection in combination with the linear stability. The quantity \( c_s(\mu) \) represents, like before, the stationary solution in the limit \( t \to \infty \). Apart from the trivial solution \( c_s = 0 \) there exists a non-trivial, memory controlled solution

\[
c_s(\mu) = \frac{1 + \mu c_0}{1 + \mu} \quad .
\]

(29)

Notice that this result is in accordance with the general conclusion expressed by Eq. \( (22) \). The stationary solution, Eq. \( (29) \), depends on both, the initial value \( c_0 \) and the memory strength \( \mu \). If one applies the Laplace transformation in Eq. \( (3) \) and making linear stability analysis, see the subsequent subsection one ends up only with the memory independent fixed points \( c_s = 1 \) (stable) and \( c_s = 0 \) (unstable), respectively. Here, we have demonstrated that an internal feedback leads to a modified non-trivial stationary fixed point. Because \( c(t) \) is a concentration the stationary solution is only accessible in case \( c_s \geq 0 \). The non-Markovian behaviour is apparent by the dependence of \( c_s(\mu) \) on the initial concentration \( c_0 \) and on the memory parameter \( \mu \).

**B. Phase diagram**

In this subsection the phase diagram is obtained employing a linear stability analysis. Notice that it can not be performed in terms of \( \varphi(z) \) defined in Eq. \( (28) \). Instead of that we have to insert \( c(t) = c_s(\mu) + \varphi(t) \) in Eq. \( (25) \). As the result one finds \( \varphi \propto \exp(-\Lambda t) \), where the stability exponent \( \Lambda \) reads

\[
\Lambda = \begin{cases} 
-1 & \text{if } c_s = 0 \\
\frac{c_0 \mu^2 + 2 c_0 \mu + 1}{1 + \mu} & \text{if } c_s \neq 0
\end{cases}
\]

(30)

The phase diagram is defined in the \( \mu-c_0 \)-plane under exclusion of the trivial case \( c_0 = 1 \). In the stable region both conditions, \( c_s > 0 \) and \( \Lambda > 0 \), has to be fulfilled simultaneously. Notice
that there exits regions where the stationary solution is available \( c_s \geq 0 \) but not stable \( \Lambda < 0 \). The different cases are summarized in Fig. 3. The non-trivial stationary solution is stable for \( \mu > -1 \) in the interval \( 0 < c_0 \leq 1 \) and for \( c_0 \geq 1 \) in case of \( \mu \geq \mu_1 \left( c_0 \right) = -1 + \sqrt{1 - c_0^{-1}} \).

There exists a second domain where the non-trivial stationary solution should be stable. This area is limited by the lines \( \mu = -1 \) and \( \mu_2 \left( c_0 \right) = -1 - \sqrt{1 - c_0^{-1}} \) (dashed lines in Fig. 3). However, the system can not achieve this region, because the initial value \( c_0 > 1 \) leads to \( c_s(\mu) > c_0 \) in contradiction to the monotone decrease of the function \( c(t) \) as indicated by Eq. (25). We omit the discussion of the other cases with different signs of the parameter \( r \) and \( u \) in Eq. (24). The inclusion of an internal memory leads to a non-trivial stationary point which is controlled strongly by the memory parameter \( \mu \). Because the feedback is characterized by the concentration, relation Eq. (22) is violated leading to a new fixed point in comparison to the non-Markovian situation.

IV. CONCLUSIONS

In the present paper we have generalized the conventional rate equations of the reaction limited case by including memory effects. Once, the memory can be originated by external constraints which hints the particle to encounter simultaneously. As a consequence the rate of the concentration at the present time may be coupled to the rate at a previous time, where between both processes an additional delay-time \( \tau \) appears. Although the stationary point are unchanged by such kind of external delay, the dynamical behaviour to reach that fixed points is altered. This situation reminds to an additive noise coupling in stochastic processes. In case of an internal feedback the stationary solution is changed and depends on the memory coupling and the initial value. The reason for that consists of the self-organized manner inherent in the memory. The time scale of the relevant variable, the concentration, determines the time scale of the feedback. Both realizations are characterized by an explicit coupling of the rates at the observation time \( t \) and a previous time \( 0 \leq t' \leq t \) or with other words, the instantaneous changing rate of the concentration is not only determined by time-local gain and loss terms, but additionally by the changing rate in the past. Such a situation may realized whenever the reacting entities are not available simultaneously. Thus, the reaction is determined by the accumulation of the species at previous times. To capture the influence of that delay process, a memory term is included into the evolution equation.
non-Markovian part is generally found adopting projection methods of statistical mechanics. Especially, the form of the memory is suggested by analyzing glasses or anomalous diffusion in disordered media. Although we are aware, that the analytical expression of the feedback term is the most controversial point, the delay is in according to the general approach applied for chemical reactions. The memory term allows to study a real competitive situation between two non-linear terms in our evolution equation, namely the instantaneous loss term and the memory driven one. Even that kind of competition leads to the richer behaviour discussed in the present paper. Due to the memory the present and the initial times are mixed. Therefore, the system offers the possibility that the reaction process can be reduced or or speeded up. As the result we get a new stationary behaviour which differs significantly from the standard one. We believe that memory effects are also a feature of other dynamical complex systems.

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FIG. 1: Stability domain for an exponential kernel in the $(\mu, \lambda, c_0)$ plane.

FIG. 2: Time evolution of $c(t)$ with a periodic kernel and $\lambda = 0.1, \mu = 1$ and $c_0 = 0.5$. 
FIG. 3: Stability of the internal memory controlled stationary solution in the $c_0 - \mu$-plane.