Memory-Controlled Annihilation Reactions

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Abstract

We consider a diffusion-limited reaction in case the reacting entities are not available simultaneously. Due to the fact that the reaction takes place after a spatiotemporal accumulation of reactants, the underlying rate equation has to be modified by additional non-local terms. Owing to the delay effects a finite amount of reactants remains localized, preventing a further reaction and the asymptotic decay is terminated at a finite density. The resulting inhomogeneous non-zero stationary concentration is stable against long wave length fluctuations. Below a critical wave vector $k_c$ the system becomes inert, whereas a complete decay is realized above $k_c$. The phase diagram for the one species-annihilation process $A + A \rightarrow 0$ exhibits a behavior comparable to a second order phase transition. Obviously the memory effects are equivalent to long range interaction and the non-local kinetics is basically independent on space dimensions.

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I. INTRODUCTION

In case the typical transport time $\tau_D$ of reacting entities is much larger than the reaction time $\tau_R$, the reaction process is affected by spatial correlations. Consequently the global concentration $c(t)$ has to be replaced by a local density function $c(r,t)$. When the reaction occurs within a cell, centered around the position $r$, the classical mean-field rate evolution equation is completed by a diffusive term, which disposes of low dimensional fluctuation corrections. The influence of such fluctuations on the long time behavior had been demonstrated in a series of papers [1], for a recent review see [2]. The newly emerging nonequilibrium behavior is extracted using more sophisticated methods as field theoretic treatment [3] or extensive numerical simulations [4]. In the one species-annihilation process a particle $A$ is annihilated upon encounter according to the reaction scheme $A + A \rightarrow 0$. The reaction, realized with a certain rate $u$, takes place immediately. The time evolution of the local concentration $c(r,t)$ satisfies the rate equation

$$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t) - uc^2(r,t)$$ (1)

Suppose that $l$ is a typical length scale until reactants meet and $\bar{c} \simeq l^{-d}$ a typical concentration in that region, the condition $\tau_D \gg \tau_R$ leads to

$$l^{2-d} \gg \frac{D}{u}$$ (2)

Since the diffusion constant $D$ and the reaction rate $u$ become fixed by microscopic processes, the spatial variation of the concentration on the length scale $l$ should be relevant for $d < 2$. Due to the short reaction time $\tau_R$ the particles annihilate very rapidly. Therefore a subsequent reaction can only take place in turn the particles has passed through the distance $l$. This effect slows the density decay down. Asymptotically one finds $c(t) \sim t^{-d/2}$ for $d < 2$ and logarithmic corrections at the critical dimension $d_c = 2$ [5]. Recently, the result has been generalized to multispecies pair annihilation leading to a modified exponent for the asymptotic decay [6]. In the opposite case $d > 2$, spatial fluctuations are irrelevant and the mean-field equation provides a valid description. The diffusion-limited reaction Eq. (1) is based on the assumption that the reactants are available simultaneously. In the present paper we emphasize, that the generic behavior of the system may be changed when additional nonlinear delay effects are included into the consideration. In particular, we discuss a reactions
which takes place after a sufficient accumulation time and after cumulating reactants within a spatial region. Under that conditions the reaction time scale $\tau_R$ is modified and likewise Eq. (2) is changed. Accordingly we demonstrate, the long time behavior is dominated apparently by the delay effects. The system is able to reach a stationary state with a finite concentration instead of exhibiting an algebraic decay in time as it follows using Eq. (1). Although the crucial factors governing the dynamics of systems, comprising many "units", consists of interaction and competition, there is an increasing interest to include memory effects as a further unifying feature of complex physical \[7, 8\] as well as biological systems \[9\]. Our model can be grouped into the effort to discuss delay and feedback mechanism. It is well-known that evolution equations with memory kernels can be derived following the well established projector formalism due to \[10\], see also \[11\]. That approach had been applied successfully for the density-density correlation function studying the freezing processes in undercooled liquids \[12, 13\]. Recently a Fokker-Planck equation with a non-linear memory term was used to discuss anomalous diffusion in disordered systems \[14\]. The results could be confirmed by numerical simulations including diffusion on fractals \[15\], see also \[16, 17\]. Moreover, it was argued \[18\] 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 \[19\]. The non-Gaussian fluctuations of the asset price can be also traced back to memory effects \[20\]. An additional cumulative feedback coupling within the Lotka-Volterra model, which may stem from mutations of the species or a climate changing, leads to a complete different behavior \[21\] 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 behavior and the phase diagram is completely dominated by such a term \[22\]. Whereas the feature of the approach, proposed in those papers, consists of self-organization, i. e. the time scale of the memory is determined by the relevant variable itself, for instance the concentration, there is a broad class of models with external delay effects \[23, 24, 25\], for a survey and applications in biology see \[26\]. That case is characterized by a given external memory kernel. The differences of both approaches will be discussed also in \[27\]. The spreading of an agent in a medium with long-time memory, which can model epidemics, is studied in \[28\]. Time-delayed feedback control is an efficient method for stabilizing unstable periodic orbits of chaotic systems \[29\]. Time
delay may induce various patterns including travelling rolls, spirals and other patterns. The influence of a global feedback is studied recently in a bistable system, where 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 time-non-locality in the equation of motion for the reduced density operator. 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 discuss the influence of a non-Markovian memory term on chemical reactions. The retardation effects are characterized by memory kernels, which are chosen in such a manner, that they compete with the conventional diffusion and the instantaneous non-linear reaction terms.

II. MODEL

Although a chemical reaction is characterized by non-linear reaction terms, as it is indicated in Eq. (1), the reaction process may be further modified when the reaction takes place after an accumulation time. In that case the time evolution of the concentration could also depend on the history of the sample to which it belongs, i.e. the changing rate of the concentration should be influenced by the changing rate in the past. Thus the evolution for global concentration $c(t)$ has to be supplemented by memory terms. Such term model, 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 loss term as well as on the changing rate at former times $t'$. Consequently the evolution Eq. (1) should be modified according to

$$\partial_t c(r, t) = \nabla^2 c(r, t) - u c^2(r, t) - \int_0^t dt' \int_{-\infty}^{\infty} dr' K(r - r', t - t'; c)$$

(3)
As the main ingredient we assume that the kernel $K$ is determined by the concentration $c$ and its derivative. With other words, the time and the spatial scale of the memory is governed by the spatiotemporal scale of the concentration. Under that conditions the chemical reaction becomes obviously a many-body problem. The reaction species are embedded into an environment of all the other particles of the system which give rise to feedback and memory effects.

Let us now specify the memory kernel introduced in Eq. (3) by the expression

$$\partial_t c(r, t) = D \nabla^2 c(r, t) - \mu \int_0^t dt' \int_{-\infty}^{\infty} dr' \nabla c(r - r', t - t') \cdot \partial_t \nabla c(r', t')$$

The second term on the right hand side characterizes a delayed diffusion with diffusion parameter $\mu$. This term conflicts to the conventional local diffusive one with the parameter $D$. Large concentration fluctuations at both times $t$ and $t'$ contribute to the behavior of the system. Different to the constant $D$ the sign of the parameter $\mu$ can range between positive and negative values. Likewise the third and the fourth term exhibit an extra competition between the local and the accumulated as well as the delayed reaction, where we assume $u \geq 0$ and $\lambda$ arbitrary positive and negative. Using scaling analysis it is easy to verify that the last term with the coupling parameter $\lambda$ is relevant in all dimensions. In contrast the spatial dependence of the local $u$-term is only relevant for $d < 2$. The diffusion term and the delayed diffusion term are of the same order of magnitude. Following the line resulting in Eq. (2), we can estimate the characteristic time scales. Whereas the diffusion time remains unchanged, $\tau_D \simeq l^2/D$, there occurs an effective reaction time $\tau_R$ which is composed of the parameters $\mu$, $u$ and $\lambda$ of the three non-linear processes, introduced in Eq. (4). The effective reaction time is fixed by

$$\tau_R \simeq \frac{1}{l^d \lambda + l^{d-2} \mu} \left[ u + \sqrt{u^2 + l^d (l^d \lambda + \mu l^{d-2})} \right]$$

The condition $\tau_D \gg \tau_R$ yields

$$\lambda l^4 + \mu l^2 + l^{2-d} Du \gg D^2.$$

In the special case $\lambda = \mu = 0$ this relation leads anew to Eq. (2). For non-zero memory parameters $\mu$ and $\lambda$ Eq. (5) is fulfilled in each space dimension. Insofar, the memory mimics
a kind of very long-range forces. In the forthcoming section, we search for the stationary solutions in arbitrary dimensions \(d\).

III. STATIONARY CONCENTRATION

In this section we show that the asymptotic behavior of the concentration is changed significantly when the retardation effects are taken into account. Firstly let us consider the case of vanishing memory parameters \(\mu = 0\) and \(\lambda = 0\). In mean-field approximation the density decay obeys \(c \sim 1/ut\). For \(d < 2\) the density fluctuations leads to an additional time dependence of the parameter \(u \rightarrow u(t)\). The explicit time dependence of \(u\) can be estimated easily by scaling arguments. The parameter \(u\) scales as \(u \sim l^{1-z}\) where the dynamical exponent \(z\) is related to the time scale by \(l \sim t^{1/z}\). Because for conventional diffusion the dynamical exponent is \(z = 2\) we find \(u(t) \sim t^{d/2-1}\) which leads immediately to the asymptotic relation \(c(t) \sim t^{-d/2}\) in accordance with more refined methods \[5\], compare also \[2\]. All particles are annihilated due to the reaction. This picture is changed, when the delay effects are enclosed into the consideration. The asymptotic behavior in time is obtained by applying Laplace transformation. Moreover let us perform Fourier transformation with respect to the spatial coordinate \(r\). The concentration after both transformations is denoted by \(c(k, z)\). Making the ansatz \(c(r, t) = g(r) + \varphi(r, t)\) or

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

where \(\varphi(k, z) = \mathcal{L}\{\varphi(k, t)\} = \int_0^\infty \varphi(k, t) \exp(-zt)dt\) should not display a singular behavior for \(z \to 0\). Inserting Eq. (7) into Eq. (4) the singular part yields the stationary solution \(c_s(k)\) which obeys the equation

\[
c_s(k) = \frac{c_s(k)[(\lambda - \mu k^2)c_0(k)] - ub(k)}{Dk^2 + (\lambda - \mu k^2)c_s(k)}
\]

with \(b(k) = \int \frac{d^d q}{(2\pi)^d} c_s(q) c_s(k - q), \quad c_0(k) \equiv c(k, t = 0)\) \(8\)

This relation has always the solution \(c_s(k) = 0\) which corresponds to a complete decay, ending up with zero concentration. In addition to this trivial solution Eq. \(8\) exhibits a non-zero stationary solution, although the instantaneous decay process, manifested the decay rate \(u \neq 0\), is still present. Obviously the memory effects prevent a complete reaction.
The non-trivial solution of Eq. (8) depends on the initial value \( c_0(k) \) and on the parameters of the model. A linear stability analysis in terms of \( \varphi(k, t) \), Eq. (9), leads to

\[
\dot{\varphi}(k, t) = -\Lambda(k)\varphi(k, t) - 2u \int_q c_s(k - q)\varphi(q, t)
\]

with \( \Lambda(k) = Dk^2 + (\lambda - \mu k^2)c_s(k) \) (9)

To discuss the generic behavior let us firstly study the case \( u = 0 \) which is reasonable, since the inhomogeneous stationary solution is originated mainly by the memory terms proportional to the coupling parameters \( \mu \) and \( \lambda \), respectively. In that case the nontrivial stationary solution reads in according to Eq. (8)

\[
c_s(k; u = 0) = c_0(k) - \frac{Dk^2}{\lambda - \mu k^2}
\]

(10)

If \( \lambda = 0 \) it results a homogeneous solution as expected whenever the initial concentration is likewise homogeneous. In general the stationary solution is only accessible when \( c_s(k) \geq 0 \) and reasonable if \( c_s(k; u = 0) \leq c_0(k) \). Because the asymptotic behavior depends essentially on the signs of the feedback parameters \( \mu \) and \( \lambda \) we consider firstly the case of \( \mu \geq 0 \) and \( \lambda \geq 0 \). For positive parameters \( \mu \) and \( \lambda > 0 \), the inhomogeneous stationary solution is stable and reasonable for \( k < k_c \) where the critical wave vector is determined by

\[
k_c^2 = \frac{\lambda c_0(k_c)}{D + \mu c_0(k_c)}
\]

(11)

A simple realization is given for \( c(r, t = 0) = c_0\delta(r) \) leading to \( c_0(k) = c_0 \). In that case the critical wave vector is simply defined by the last equation where \( c(k_c, 0) \) is replaced by \( c_0 \). Remark that the critical value \( k_c \) fulfills the relation \( k_c < \sqrt{\lambda/\mu} \) In this manner the spurious singularity in Eq. (10) is avoided. Together with the stability criteria \( \Lambda(k) > 0 \) we get the phase diagram depicted in Fig.1. The curve is similar to the behavior of a second order phase transition. Introducing the variable \( w = k/k_c \) we get

\[
c_s(w; u = 0) = (1 - w^2)\frac{c_0(D + c_0\mu)}{D + c_0\mu(1 - w^2)}
\]

(12)

One can study the spatial dependence of non-trivial behavior of \( c_s(r) \) by making the inverse Fourier-transformation. For large \( r = |r| \to \infty \) we get

\[
c_s(r) = c(r, 0) - \frac{\kappa}{r^{d+2}}
\]
where $\kappa$ is a factor depending on the parameters of the model. The physical behavior of the system can be discussed in terms of particles and holes denoted as $A$ and $B$ particles, respectively. On a large length scale the final state of the system consists of homogeneous distributed $A$-particles, which becomes inert and which are separated from the holes. On a short scale the $A$-particles disappear further until they are completely annihilated and only holes leave over. The systems exhibit a new kind of phase separation mechanism.

In the same manner we can discuss the residual cases with varying signs of the feedback parameters $\mu$ and $\lambda$. If both parameters are negative, $\mu < 0$ and $\lambda < 0$, we find the inverse situation compared to that one discussed above. A non-zero stable and simultaneously reasonable stationary state appears for $k > k_c$, whereas for $k < k_c$ all the particles undergo the complete reaction, see Fig. 2. The system exhibits a microphase-separation. It decays in small subunits of extension $l < k_c^{-1}$. If $\mu > 0$ and $\lambda < 0$ there exists only the trivial stationary solution $c_s(k) \equiv 0$. In the remaining case, $\mu < 0$ and $\lambda > 0$, we find a stable non-zero stationary solution for all wave vectors provided the initial concentration fulfills the condition $c_0(k) > D|\mu|^{-1}$. In the opposite case one observes a similar behavior as it is depicted in Fig. 1.

If the reaction parameter $u$ is non-zero, Eq. (8) can not be solved exactly due to the non-linear convolution term. However, the main conclusions remain valid, in particular for a small coupling parameter $u$. In a linear approximation with respect to $u$ the stationary solution Eq. (10) is modified in according to $c_s(k; u = 0) \to c_s(k; u) \equiv c_s(k; u = 0) - u R(k)$ with

$$ R(k) = \int \frac{d^dq/(2\pi)^d}{(\lambda - \mu k^2) c_s(k; u = 0)} c_s(q; u = 0) c_s(k - q; u = 0) $$

Expanding the last expression with respect to $k^2$ by using Eq. (10) we find, that the critical wave vector $k_c$, compare Eq. (11), is slightly reduced and the stability of the solution is maintained. The phase diagram, presented in Fig. 1, is preserved.

IV. CONCLUSIONS

In this paper we have extended the conventional modeling of chemical reactions by including non-Markovian memory terms within the evolution equation. The additional terms give rise to a competitive behavior for both the local reaction and the diffusive transport term. The influence of the feedback-couplings is essential, in particular in the long time limit. Due
to the memory effects the reactants may be localized and therefore a further reaction is prevented. The resulting asymptotic inert state is stable on a large length scale. However, there exists a critical wave vector, above it, the reaction can be continued as long as all the reacting particles are annihilated completely. The reason for such a new behavior is by means of an explicit coupling of the rate of the concentration at the observation time $t$ to that one at a previous time. This time accumulation is further accompanied by an additional spatial accumulation, the effect of which is comparable to the effect a long-range interaction forces and consequently the results are basically independent on spatial dimensions in according to scaling arguments. These many-body effects are shown to change the asymptotic behavior drastically. Due to the feedback-coupling of a particle to its environment, a subsequent particle, undergoing a diffusive motion, gains information from a modified environment. Hence the particle can be confined within a certain region preventing a further reaction. In this manner a self-organized memory leads to a non-zero stationary concentration $c_s(r)$, where the analytical form of $c_s$ is controlled by the memory strength. This situation is realized on a large length scale. Below a critical wave vector $k_c$ the inhomogeneous stationary solution is stable. The phase diagram is similar to an equilibrium phase transition of second kind. The model could be relevant for very complex chemical reactions where not all entities are present simultaneously.

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FIG. 1: Stationary concentration $c_s(k)$ versus $w = k/k_c$ for positive parameters $\mu, \lambda > 0$

FIG. 2: Stationary concentration $c_s(k)$ versus $w = k/k_c$ for negative parameters $\mu < 0$ and $\lambda < 0$