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LIMITS OF KINETIC SCHEMES FOR EXCITON REACTIONS

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Abstract - In this communication we analyze exciton annihilation reactions under spatial constraints. Such limitations often lower the effective dimension, an aspect which can be well-modelled through fractals. Thus, qualitative deviations of the reaction pattern from the kinetic scheme occur and allow to highlight the limits of the kinetic approach.

Excitons are prone to relax through a whole game of reaction patterns, many of which do not lead to the exponential decay laws typical for intrinsic lifetime processes. Envisaging mobile species, the reactive encounters may involve excitons of the same type (here the triplet deactivation $T + T \rightarrow S$ is an example), or excitons of different types $(S,T)$ or excitons and impurities (traps). Because of the encounter aspect, it is tempting to view such deactivation processes as the chemical reactions $A + A \rightarrow P$ or $A + B \rightarrow P$ and to use kinetic schemes in describing the exciton decay /1/.

It must be realized, however, that the description of reacting species through differential equations for the number of particles, i.e. the kinetic scheme, is based on the implicit assumption of a well-stirred reactor /2/. This presupposes that the particle distribution is homogeneous at all times, an assumption which simplifies considerably the underlying many-body problem, in which the motions and reactions of all particles are correlated. For simple reactions the kinetic equations are readily solved; thus, for time-independent rates the $A + A$ reaction shows a $1/t$ behavior at longer times, whereas the $A + B$ reaction is richer; for an equal number of $A$ and $B$ excitations the decay follows the $1/t$ pattern, whereas for $A(0) \ll B(0)$ the decay of the minority species is quasiexponential /2/.

Homogeneity conditions are often violated, either already initially, or through the process of the reaction, which can enhance local density fluctuations. That such limitations do not completely disrupt the kinetic approach is due to its use for particles moving in three-dimensions, in which case the deviations are relatively small and occur at long times. The situation changes, however, when spatial restrictions limit the allowed motions, in which case the kinetic scheme is not any longer appropriate; such restrictions may be motion on surfaces or along preferred axes or in a tortuous medium.

To exemplify the above let us start with the reaction $A + B \rightarrow B$, in which the $A$-excitation disappears when encountering a $B$-species. For static $B$-particles this corresponds to the trapping problem, in which the $A$ are trapped by the $B$ and deactivate /3,4/. On the other hand, when only the $B$ are allowed to move, the $A$ play
the role of targets /5-7/. As we have shown recently the target problem admits an exact solution in all dimensions /7/; the solution reflects the spatial restrictions of the motion, and follows the exp \([-CS(t)]\) form, where \(C\) is a constant and where for large \(t\):

\[
S(t) \sim \begin{cases} 
\sqrt{t} & (d=1) \\
\sqrt{t/\ln t} & (d=2) \\
t & (d=3)
\end{cases}
\] (1)

Tortuous systems, such as glasses or porous rocks may be modelled through fractals /8-10/, geometrical objects without translational symmetry, whose dimension is not necessarily integer. For fractals the target decay also follows exp \([-CS(t)]\) where now for large \(t\) /7/:

\[
S(t) \sim \begin{cases} 
\sqrt{\bar{d}/2} & (\bar{d}<2) \\
1 & (\bar{d}>2)
\end{cases}
\] (2)

\(\bar{d}\) being the spectral (fracton) dimension.

On the other hand, the trapping problem is more complex, and an analytical solution is known /3/ only for \(d=1\). In the general case, at moderate times, the decay can be expressed through a cumulant-expansion /4/, which asymptotically turns to /11/\[
\exp \left[-ct^{d/(d+2)}\right].
\]

The distinction between the target and the trapping problem unveils a fundamental aspect, namely that the course of the reaction depends on which of the species moves. This distinction is lost when reactions are treated in a pair-approximation scheme, which focusses on one A and one B particle and in which only the sum \(D = D_A + D_B\) of the diffusion coefficients enters /12/. Truly, the solution of a diffusion equation with a sink term leads to time-dependences such as given by Eq. (1), but these may be only the leading terms of a complex random-walk expression. Here one encounters the fact that a random-walk problem is not necessarily reducible to simple diffusion.

As a proof we display in Fig. 1 the decay of A-excitations distributed on a surface (square grid). To simulate a realistic situation, we also allow both the A- and B-species to move, and distribute the mobilities \(m_A : m_B\) according to 0 : 1, 0.5 : 0.5, 0.75 : 0.25, 0.9 : 0.1 and 1 : 0. The special cases 0 : 1 and 1 : 0 correspond to the target and to the trapping problems, respectively, between which the intermediate \(m_A : m_B\) interpolate. We obtain the decay \(\Phi_n^A\) as a function of the number of steps \(n\), which is distributed according to \(m_A : m_B\) over the A and B moieties. Thus, for each initial concentration \(p_B\) of the B species (we chose \(p_B = 0.2\) and \(p_B = 0.5\)) the diffusion-picture based on \(D_A + D_B\) predicts the same decay, in contrast to the findings of Fig. 1.

The picture becomes more drastic for lower dimensions, since there the difference between the target and the trapping forms grows. In Fig. 2 we present the decay \(\Phi_n^A\) for A- and B-species moving on a Sierpinski-gasket /8/ embedded in the two dimensional Euclidean space. For this fractal \(\bar{d} = 2 \ln 3/\ln 5 = 1.365\). The values of \(m_A : m_B\) are 0 : 1, 0.9 : 0.1, 0.95 : 0.05, 0.98 : 0.02 and 1 : 0. Here again the motion of the B-species enhances the decay. In an intuitive way, one may view the motion of the species unaffected by the reaction as an internal stirring process, which, in the extremely rapid limit (unobtainable in \(d < 2\) by simple diffusion) leads to the exponential forms of the kinetic scheme.

To push the point still further, we show in Fig. 3 the corresponding decays for A- and B-species distributed on a chain (\(d=1\)), with \(m_A : m_B\) being 0 : 1, 0.5 : 0.5, 0.75 : 0.25 and 1 : 0. Here not only the target but also the trapping solutions are known exactly, as indicated in the Figure. Again, the decays are distinct. As a side remark, one may notice that in dimensions \(d\neq 1\) the curves for intermediate \(m_A : m_B\)
Fig. 1 - The time dependence $\Phi_n^A$ of the A-excitations deactivated by B-species, $A + B + B$, where both species are initially randomly distributed on a square lattice. The steps occur according to the mobility ratios $m_A : m_B$, which range from $0:1$ (target) to $1:0$ (trapping). The exact target-problem result is given through a dashed line.

Fig. 2 - The decay $\Phi_n^A$ as in Fig. 1, but now having as underlying grid a fractal, the Sierpinski-gasket, with $d = 1.365$. 
values lie rather closely to the target decay, whereas in $d=1$ the singular role of the trapping form is less pronounced.

![Graph showing decay $\Phi_n^A$ as a function of $n$ for different values of $d$.](image)

Fig. 3 - The decay $\Phi_n^A$ as in Fig. 1, but now the motion is restricted to a linear chain. Here both the target and the trapping solutions are known exactly and are indicated as dashed lines.

In order to discuss the role of density fluctuations we center now on the annihilation reactions $A + A \rightarrow 0$ and $A + B \rightarrow 0$, with $A(0) = B(0)$. Although one may intuitively expect the former to be more influenced by fluctuations /13/, it turns out that the opposite is the case /2/. Interestingly, the $A + A \rightarrow 0$ annihilation pattern follows $1/S(t)$ with $S(t)$ given by (1) and (2). Thus, the geometrical restrictions are still felt, but above $d=2$ the kinetic scheme is indeed justified. On the other hand the strictly bimolecular reaction $A + B \rightarrow 0$, $A(0) = B(0)$ is dominated by density fluctuations, which get enhanced in the process of the reaction /2,14,15/. Thus, in Fig. 4 we display the distribution of A and B particles on a Sierpinski-gasket, following an initially random particle distribution, after $10^5$ steps have elapsed. One sees large, well separated regions, in which only excitations of one kind are present. The reaction is now slowed down by the fact that only particles at the region boundaries are prone to react. At long times the decay obeys a $t^{-d/4}$ law instead of a $t^{-d/2}$ behavior /2,14,15/. Thus, here the kinetic scheme is expected to hold only above $d=4$.

In summary, we have analyzed reaction patterns common in exciton annihilation processes and have shown that in low dimensions approximate methods such as the kinetic scheme, or even the more sophisticated diffusion approach, lead to relaxation forms which are qualitatively at variance with the analytical and numerical findings. These discrepancies are less evident in three dimensions, possibly the reason why the above approximations were seldom challenged.
Fig. 4 - Distribution of the A and B excitations under bimolecular-type annihilation, $A + B \rightarrow 0$, on a Sierpinski-gasket, for an initially equal number of excitations, $A(0) = B(0)$. Pictured is the situation after $\sim 10^2$ steps.

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