MODELING OF SINGLET–SINGLET ANNIHILATION IN MOLECULAR LATTICE

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Introduction

Singlet–singlet annihilation is a common phenomenon in molecular structures. It is often difficult to provide experimental conditions that could prevent annihilation; therefore, it might often be necessary to account for it while analyzing data.

Simple annihilation model can be described by rate equation:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\gamma n^2,$$

here $n(t)$ is the mean number of remaining excitations in the system at time t and γ is the rate constant for annihilation. To account for both finite transfer rate and discrete number of excitations in annihilation model, we have chosen to use Monte Carlo method and continuous time random walk algorithm. In this work the copmarison of excitation population kinetics in one-dimensional, two-dimensional and three-dimensional lattices is provided, followed by analysis by approximating kinetics using statistical approach and kinetic equation:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\gamma(t) \cdot n^2(t) - k_{rel} \cdot n(t),$$

here k_{rel} is relaxation rate.

Algorithm

The algorithm is based on continuous time random walk. At each time step, for every excitation (randomly distributed in the lattice) an interevent time is calculated as a random number from exponential distribution with mean μ:

$$T = -(\ln r) \cdot \mu$$

where r is a uniform random variable on $[0, 1]$. The excitation with the shortest interevent time generated will now have one of two fates: moving to another position with probability to annihilate or relax to the ground state.

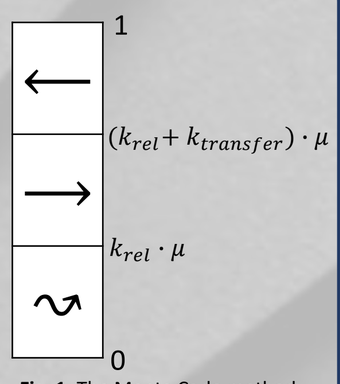

Fig. 1. The Monte Carlo method

The next part of the algorithm is based on Monte Carlo method. The fate of the excitation depends on a randomly generated number from 0 to 1, as shown in the picture. If the excitation moves, there is a possibility that the site it has moved to will already be occupied. In that case, all but one excitations relax from that node as for annihilation. The process is repeated by generating new interevent times for excitations that are left.

Eventually, number of excitations in the lattice becomes zero and the process is repeated by generating new initial distribution of excitations. After 1 000 000 lattices have been generated, the average kinetics is calculated considering that initial distribution of excitations obeys a Poisson distribution. The algorithm can calculate average excitation population kinetics using various sizes of initial populations and various sizes of the lattice.

Approximation using the statistical approach

The same five annihilation rate time dependences (see Table 1) were chosen for approximation using the statistical approach. For every $\gamma(t)$, the best values of γ_0 and τ are presented in the table below. Here the size of the lattice is 100 nodes and the initial excitation population size is $n_0 = 20$. The best fit of the statistical approach is obtained with the second annihilation rate time dependence. Graphical representation of this approximation is shown in the picture below.

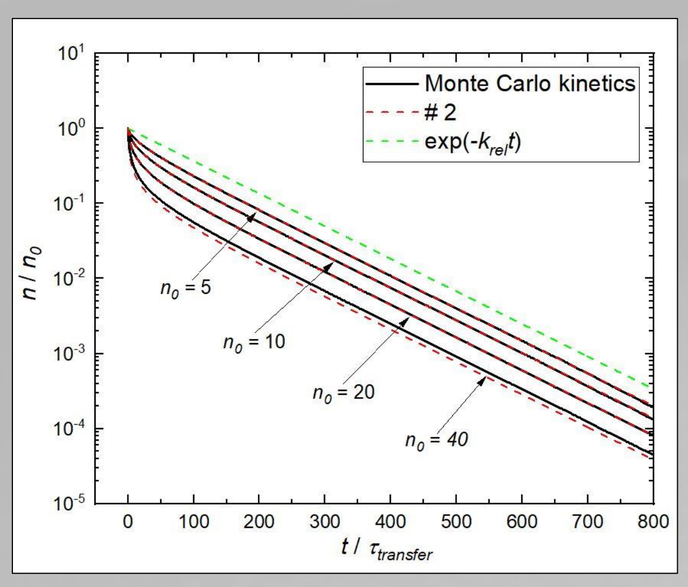

Fig. 4. Statistical approach approximation using $\gamma(t)$ that provides the best fit.

Table 3. Parameter values obtained during statistical approach approximation.

№	γ_0	τ	Sum of squares
1	0.018044	-	8.527232
2	0.060871	0.146336	0.006581
3	0.030425	0.498047	0.082564
4	0.037279	0.377192	0.008885
5	0.02678	0.637753	0.104969

Conclusions

- Singlet-singlet annihilation in molecular structures can be described using Monte Carlo method and continuous time random walk algorithm.
- In two-dimensional and three-dimensional lattice excitation quenching due to annihilation is more rapid than in one-dimensional lattice.
- Monte Carlo kinetics can be approximated using both kinetic equation and statistical approach.

Statistical approach

While using statistical approach, molecular aggregate is considered to be one supermolecule and excitation dynamics are characterized by its energy levels. The relaxation process in this case can be described by the Master equation:

$$\frac{\partial}{\partial t} P_i(t) = -\left(i \cdot k_{rel} + \frac{\gamma(t)}{2} i(i-1)\right) P_i(t) + \left((i+1) k_{rel} + \frac{\gamma(t)}{2} i(i+1)\right) P_{i+1}(t),$$

here $P_i(t)$ is a probability that at time t there are i excitations in the molecular system, k_{rel} is relaxation rate, $\gamma(t)$ is time dependence of annihilation rate. The average number of excitations present at time t is given by:

$$n = \sum_{i=0}^{n_0} i \cdot P_i.$$

Here n_0 is the initial number of excitations in the molecular aggregate.

Kinetics in 1D, 2D and 3D lattice

The model is set to calculate excitation dynamics in one-dimensional, two-dimensional and three-dimensional lattices. In the figure below kinetics of two different initial population sizes are presented. For both models, the number of nodes in the lattice was the same ($N = 100$). One can notice that in two-dimensional lattice excitation quenching is more rapid than in one-dimensional lattice. Although in three-dimensional lattice excitation quenching is more rapid than in two-dimensional lattice, the difference between these two is less significant compared two one-dimensional lattice.

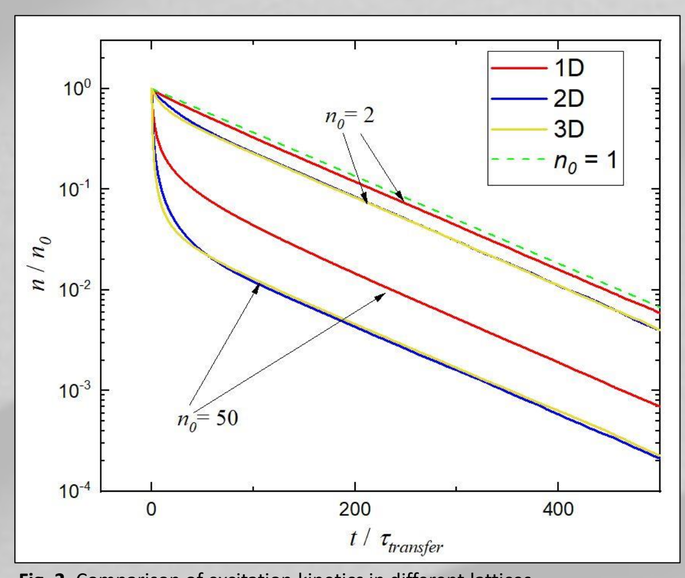

Fig. 2. Comparison of excitation kinetics in different lattices.

Fitting the kinetic equation

For a diffusion-limited process time dependence of the annihilation rate can be approximated by a power law [2]. For one-dimensional lattice we have chosen to test the following $\gamma(t)$ time dependences (for both kinetic equation and statistical approach):

Table 1. Annihilation rate time dependences.

№	$\gamma(t)$
1	$\gamma(t) = \frac{\gamma_0}{\sqrt{t}}$
2	$\gamma(t) = \frac{\gamma_0}{1+\sqrt{t/\tau}}$
3	$\gamma(t) = \frac{\gamma_0}{\sqrt{1+t/\tau}}$
4	$\gamma(t) = \gamma_0\left(1 - \exp\left(-\sqrt{\tau/t}\right)\right)$
5	$\gamma(t) = \gamma_0 \tanh\left(\sqrt{\tau/t}\right)$

Table 2. Parameter values obtained during kinetic equation approximation.

№	γ_0	τ	Sum of squares
1	0.008494	-	6.319613
2	0.03879	0.071238	0.177116
3	0.017795	0.301208	0.071339
4	0.021464	0.236729	0.202331
5	0.015566	0.391872	0.07121

For every annihilation rate time dependence, the best values of γ_0 and τ are presented in the table above. One can notice that the best fit of kinetic equation can be obtained with the fifth $\gamma(t)$ dependence followed by the second best fit with the third $\gamma(t)$. The difference of sum of squares is almost insignificant and is proportional to 10^{-4}. The values in the table were obtained by fitting the kinetics in one-dimensional lattice of 100 nodes and with 20 initial excitations in the system. Kinetic equation fitting while using various initial number of excitations is graphically presented in the picture below.

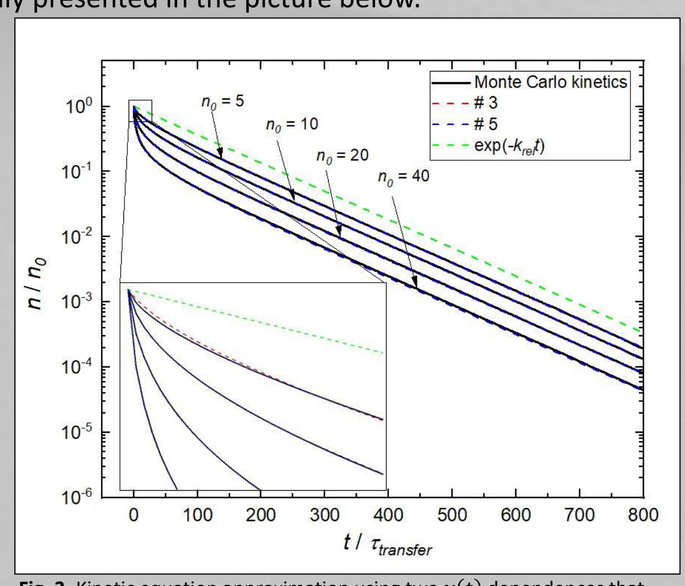

Fig. 3. Kinetic equation approximation using two $\gamma(t)$ dependences that provide two best fits

References

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[2] V. Barzda, V. Gulbinas, R. Kananavicius, V. Cervinskas, H. van Amerongen, R. van Grondelle, L Valkunas, Singlet-Singlet Annihilation Kinetics in Aggregates and Trimers of LHCII, Biophys. J. 80, 2409–2421 (2001).