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# PRINCIPLES OF MONTE CARLO SIMULATIONS IN PHYSICAL CHEMISTRY: LUMINESCENCE OF ORGANIZED DYE MOLECULES

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**Abstract.** The student computer class presented in this paper demonstrates how to apply the principles of Monte Carlo (MC) simulations to study some chemical and physical processes in the Physical chemistry discipline. In particular the principles of MC simulations are demonstrated by several examples oriented on luminescence decay analysis of organized dye molecules: simulation of fluorescence decay, simulation of energy transfer (EnT) process, fluorescence decay fitting, simulation of the pyronine (Py<sup>+</sup>) fluorescence emission in the Py<sup>+</sup>-zeolite L material. This computer class is a good tool for introducing the MC technique to the students and provides a considerable feeling on the fluorescence spectroscopy method.

## 1. Introduction

Many educational experimental fluorescence techniques for undergraduate student laboratories have been developed to provide reliable, convenient and high-precision information on different chemical and physical phenomena in physical chemistry [5,6]. However, the goal of the computer classroom paper presented here is to teach students of physical chemistry and chemistry specialties how to perform computer statistical experiments using the principles of MC simulations [3]. Since MC experiments are very intuitive and simple to implementing on a computer they can be used to study important photophysical properties of luminescent dyes, e.g. the distribution of dyes in excited states, the fluorescence emission, EnT properties in donor-acceptor molecular systems. In this paper we address the MC computer class to the study of the luminescence properties of organized dye molecules in the presence of EnT process between them.

The first theory of EnT was developed by Förster and it was based on the assumption of a weak interaction between the transition dipole moments of the molecules participating in the EnT process [7]. Afterwards Dexter generalized this theory including multipole- and exchange interactions. One of the most efficient non-analytical methods that in principle can describe the EnT processes in complex molecular systems is the MC method. The main advantage of simulating EnT by means of MC simulations is that it allows understanding straightforwardly how various parameters of a physical model affect the outcome or so-called experimentally-detected properties of the system, e.g. the time-resolved absorption and fluorescence spectra. In this paper we show by supplemented MathCAD programs the use of the MC principles for approximating the value of  $\rho$ , for modeling the luminescence behavior of non-interacting dye, for studying the properties of a simplest EnT process in an idealistic donor-acceptor pair, for simulating the Py<sup>+</sup> fluorescence emission in the Py<sup>+</sup>-zeolite L material, which can be compared with the results of the real physical experiments.

## 2. Theory and Methodology

The MC methods are stochastic techniques, based on the use of random numbers and probability statistics, which provide approximate solutions to a variety of mathematical problems where in the absence of special data structure all other analytical methods have unavoidable errors. From another point of view MC simulation is also a very intuitive and didactical way helping to better understanding complex problems arising in physical chemistry by performing statistical sampling experiments on a computer. In the following we describe the principles of MC methods to simulate the luminescence of organized dye molecules by addressing several considerably simple and demonstrative examples implemented in the supplemental MathCAD programs (see Progr0.mcd, Progr1.mcd, Progr2.mcd, Progr3.mcd, and Progr4.mcd), namely: calculating the value of  $\rho$ ; simulating the fluorescence decay; simulating EnT process; fluorescence decay fitting; and simulating the Py<sup>+</sup> fluorescence emission in the Py<sup>+</sup>-zeolite L material.

We describe now the methodology used in our MC methods.

*Calculating the value of  $\mathbf{p}$ .* We start with a straight-forward example of calculating the value of  $\mathbf{p}$  to illustrate how the MC method works in principle. Let assume that we have a circle of radius  $R$  inscribed within a box. Then the ratio of the area of the circle to that of the box is given

$$\frac{s_{Circle}}{s_{Box}} = \frac{\mathbf{p}R^2}{4R^2} = \frac{\mathbf{p}}{4} \quad (1)$$

A simplest way to calculate the eqn. (1) is to randomly pick points ( $N$ ) within the box. The ratio of the number of random points falling inside the circle ( $M$ ) to the total number random points generated ( $N$ ) is equal to the ratio of the eqn. (1). Finally, to obtain an estimate for  $\mathbf{p}$  we multiply this value by factor of four.

*Simulating the fluorescence decay.* The MC method is one that can directly simulate the fluorescence decay process and data which are very closely to real fluorescence spectroscopy measurements. For example, the simplest model of the fluorescence intensity decay, as that of a low-concentration solution of non-interacting molecules, is a single exponential. Its analytical presentation is given by the exponential equation with parameters  $I_0$  and  $\mathbf{t}$ , which are being the fluorescence intensity at time 0 and the fluorescence lifetime of a dye correspondingly.

The MC simulation is performed by the generation of the time of the photon arrivals  $t_{det}$  at a detector with equation

$$t_{det} = -\mathbf{t} \ln(\text{rnd}(1)), \quad (2)$$

where  $\text{rnd}(1)$  is a generator of random numbers in the range (0,1) (the uniform distribution). The set of ( $\mathbf{F}$ ) excitations is played for one individual molecule and after generating  $t_{det}$ , the channel number, that will serve as the current accumulator of the considered event of an excitation decay, can be calculated as  $k_{det} = (t_{det}/\mathbf{Dt})$ , where  $\mathbf{Dt}$  is the time channel width of a multichannel detector. The decay times of the photon arrivals  $t_{det}$  are stored in the histogram  $I$ , which represents the simulated fluorescence decay of the dye.

*Simulating EnT process.* The MC method is often an effective approach to analyze the processes involving excitation energy transport in a variety of molecular systems [2]. Here we describe the MC methodology to simulate the fluorescence decay of donor and acceptor dyes in the presence of EnT, for example of Förster type. In this simplest molecular EnT system donor and acceptor dyes are separated by a constant distance. The distance defines the rate and mechanism of EnT. The excited donor can relax in two ways: i) spontaneous emission with the lifetime  $\mathbf{t}_D = 3$  ns at 450 nm of wavelength and ii) resonance EnT, characterized by the EnT rate constant  $k_{EnT}$ , to ground-state acceptor, which can emit at 605 nm of wavelength with the lifetime  $\mathbf{t}_A = 3$  ns. The analytical equations for the donor and acceptor fluorescence are given in ref. [1].

The MC simulation of the fluorescence decay of donor affected by the EnT to acceptor is performed as follows: The donor decay time  $t_{det}$  can be generated with eqn. (2) whereas the EnT time  $t_{EnT}$  is differently:

$$t_{EnT} = -k_{EnT}^{-1} \ln(\text{rnd}(1)), \quad (3)$$

where  $\text{rnd}(1)$  is a generator of a random number in the range [0,1] (the uniform distribution). If  $t_{det} < t_{EnT}$  then  $t_{det}$  is stored in the histogram  $ID$ , representing the donor decay, and its emission wavelength is generated using the random number generator for the normal distribution  $N(450,50)$  and is recorded in the histogram  $SP$ , representing the emission spectrum. Otherwise there is an emission of the luminescent acceptor dye

$$\mathbf{Dt}_{tA} = -\mathbf{t}_A \ln(\text{rnd}(1)) \quad (4)$$

and then  $t_{det} = t_{EnT} + \mathbf{Dt}_{tA}$  is recorded in the histogram  $IA$ , representing the acceptor decay, at the acceptor wavelength 605 nm using different random number generator  $N(605,20)$ . Running this simulation procedure  $\mathbf{F}$  times, the fluorescence decay and spectrum of donor and acceptor dyes can be collected in the histograms  $ID$ ,  $IA$  and  $SP$ .

*Fluorescence decay fitting.* This section employs a more general approach to the fluorescence decay fitting resulting in the combination of MC simulations and an optimization algorithm [2]. We demonstrate the MC fluorescence decay fitting by an example of donor fluorescence decay analysis in the donor-acceptor molecular pair as that one described in the previous section. In this MC approach so-called experimental data, presented by donor fluorescence decay  $I$ , are approximated by the synthetic data  $S$  obtained by means of MC method. The optimization procedure  $Fit$  lies inside the approximation technique. Assuming that the theoretical data  $S$  with the least number of system parameters unambiguously describes the investigated system, the best approximation of the experimental data  $I$  yields the values of  $\mathbf{t}_D$  and  $k_{EnT}$  parameters. The best approximation is also defined by a  $\chi^2$  criterion, establishing how far the simulated fluorescence decay  $S$  deviates from the experimental data  $I$ , the plots of the weighted residuals and the autocorrelation function of the weighted residuals, the plots of empiric frequency histograms of the weighted residuals and the autocorrelation function of the weighted residuals.

Note that the MC method is used for both the computer generation of the so-called experimental data as well as for the calculation of the approximating theoretical data.

*Simulating the  $\text{Py}^+$  fluorescence emission in the  $\text{Py}^+$ -zeolite L material.* The principle of a photonic bi-directional  $\text{Py}^+$ -zeolite L material and corresponding directions of radiationless electronic excitation energy migration (EM) are described in ref. [4] and their overview is presented in Fig. 1.

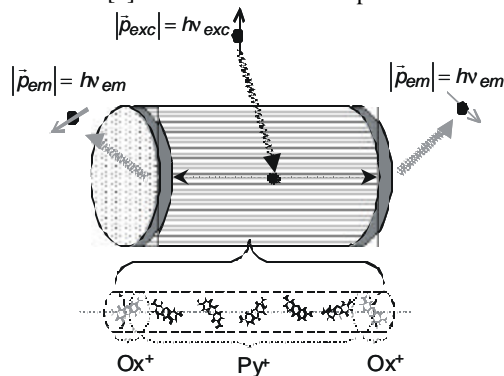


Fig. 1. Photonic acceptor,donor-zeolite L antenna system. The guest molecules,  $\text{Py}^+$ , located in the zeolite L, are excited by the incident light. The excitation energy migrates to the neighborhood and then it is emitted.

The channels of the zeolite crystal are occupied by energy transporting dyes. Having been excited by incident light, the excited dye can transfer its energy to a neighboring ground-state dye. In a series of EnT steps the excitation energy reaches either a dye at one end of the channels or it is somehow trapped on its way or escapes by spontaneous emission. Two EnT pathways, along and across the crystal channels, must be considered. Fast EM is crucial if a long distance, up to hundreds of nanometers, in a crystal should be run by excitation in a crystal before other processes take place.

The MC simulation starts from an initially excited  $\text{Py}^+$ , the excitation energy randomly walks along and across chains of dyes, i.e. along parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) directions to the main axis of the zeolite L crystal, until the event of  $\text{Py}^+$  radiative emission or falling into a trap (nonluminescent trap) happens. If the excitation is trapped by a nonluminescent trap, then it is lost. The time spent by the hopping around of the excitation energy from the moment of initial excitation until emission is considered as one run in the simulation procedure. These simulation runs are repeated many times, typically  $10^5$ – $10^6$  times, in order to obtain an appropriate value for signal to noise ratio in a theoretical decay.

### 3. Results and Discussions

*Calculating the value of  $\mathbf{p}$ .* A typical example of MC approximation of is shown in Fig. 2.

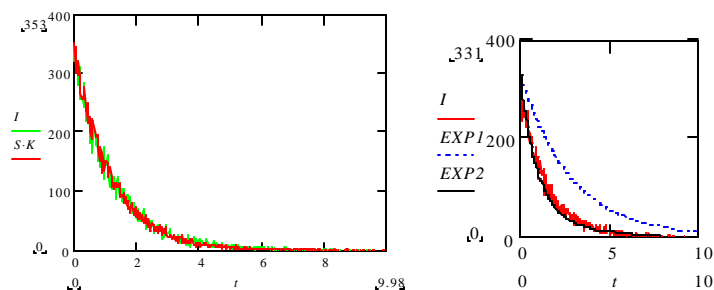


Fig. 2. Results of MC simulations. Left: The estimated  $\mathbf{p}^o$  value over the range  $(100, 10^5)$  of random points with the step of 1000.  $\text{Err} (= 10\%)$  is a value of precision. Central: Graphs of the experimental (light) and best-fitted theoretical (dark) fluorescence decays. Right: Graphs of the simulated fluorescence decay (noisy line), experimental data (solid lines) of the  $\text{Py}^+$  in the  $\text{Py}^+$ -zeolite L material and a single exponential function (dashed line) representing the experimental fluorescence decay of the  $\text{Py}^+$  in a toluene solution.

The accuracy of the value for  $p$  that we can obtain with the MC simulation depends on the number of random points generated within the box. More random points lead to a more accurate value. For example, running the program with  $N = 10^5$  gives the value of  $p$  to be  $3.1415 \pm 0.0015$ . The beauty of the MC method is that it is so simple that we can calculate  $p$  to very high accuracy by just choosing more and more points.

*Simulating the fluorescence decay.* The application of MC method to the simulation of the fluorescence decay of noninteracting dyes gives a good feeling for MC method since it is very similar to way how photon counting techniques work; see Fig. 2. The quality of MC calculation significantly depends on the number of excitations  $F$ , which is also a characteristic of signal to noise ratio, and the size  $\Delta t$  of a time channel.

*Simulating EnT process.* In the previous sections we demonstrated the basic ideas of MC calculations. The EnT process in the donor-acceptor molecular pair is more complicated. Since it involves the simulation of three processes: (i) the fluorescence emission of donor dye, (ii) EnT of the electronic excitation from donor to acceptor, and (iii) the fluorescence emission of acceptor dye. Several examples of the fluorescence decay and emission spectrum of donor and acceptor dyes for different sets of the parameters are shown in Fig. 3.

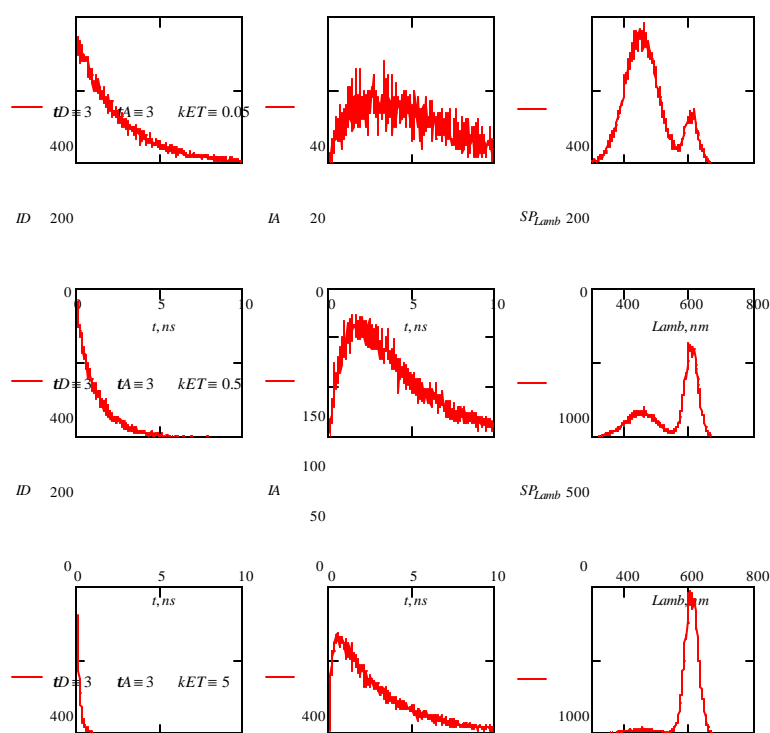


Fig. 3. Fluorescence decay of donor (Left column of plots) and acceptor (inner column of plots) and their emission spectrum (Right column of plots).

The fluorescence decay of donor at the absence of EnT to acceptor is the single exponential with the lifetime  $t_D$  and this decay becomes faster as the EnT rate is increased; see Fig. 3. The acceptor fluorescence initially increases because of the EnT from donor then it reaches a maximum before it decays to zero and it emits more strongly as the EnT rate is faster. So, the fact that the donor luminescence decays much faster versus increasing the EnT rate and that luminescence of acceptor has first to be built up before it starts to decay with a decay parameter of acceptor are beautifully supported in the MC simulations. Similar behavior is exhibited for the emission bands of donor at 540 nm of wavelength, which becomes weaker with increasing EnT, and that of acceptor dye, having been increased in the result of the EnT from donor.

*Fluorescence decay fitting.* An example of the MC fluorescence decay fitting is shown in Fig. 2. The number of function calculations  $nF$  is very important in this fluorescence decay fitting; as bigger the

value of  $nF$  – the more precisely parameters are determined. The number of simulation runs  $FS$  (or simulation counts) is also of critical importance in simulation-based fitting because it determines the signal to noise ratio. Since it is significant to minimize the computer simulation time and at the same time to reach acceptable statistics of the simulated data, the number  $FS$  of simulation runs should be carefully chosen. According to the  $\chi^2$  criterion, the best set of parameters fitted to the experimental data is that which yields a minimum for the  $\chi^2$ . For a good fit,  $\chi^2$  should be close to 1. Values above 1 mean that the quality of the fit is poor. If the  $\chi^2$  value is smaller than 1, then the curve is overfitted.

Residuals from successful fits should show a normal distribution with a mean of zero and a standard deviation of 1. The plot of the weighted residuals is a good test when gross non-randomness is present. However, it cannot resolve small non-random deviations resulting from a poor fit. The autocorrelation function of the weighted residuals is a powerful tool to find weak periodic signals in noisy data. The autocorrelation function of a successful fit should be normally distributed around zero and should show high frequency low amplitude oscillations around zero.

*Simulating the Py<sup>+</sup> fluorescence emission in the Py<sup>+</sup>-zeolite L material.* The example of the Py<sup>+</sup> fluorescence emission in the Py<sup>+</sup>-zeolite L material obtained by means of MC simulation is shown in Fig. 2. The experimental data on Py<sup>+</sup>-zeolite L materials of different loadings and the EnT parameters resulted from our MC simulations are reported in ref. [8]. Students can manipulate by the model parameters in order to organize the different loadings of Py<sup>+</sup>-zeolite L materials and corresponding MC simulated data.

#### 4. Summary

We have demonstrated that the Monte Carlo method is powerful option that enables students to solve typical problems of fluorescence spectroscopy measurements in other way, which could be carried out not only at the undergraduate student laboratory but also at a computer class. Students can do this computer class during 14-16 hours on IBM PIII PC using the MathCAD software of up to the 2001i generation. Additional time may be spent in the class for some extra-exercises advancing the students to better adopting new material. Finally, we would like to mark that the principles of Monte Carlo simulations could be extended for other more complex problems studied in physical chemistry.

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