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Two- and three-dimensional restricted geometry case of luminescence quenching

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ABSTRACT

We present general analytical expression for two and three-dimensional cases of static energy transfer kinetics in doped nanoparticles (of round, spherical and cylindrical shape). A series of numerical experiments has been performed using Monte-Carlo simulation. The analytical expressions have shown very good coincidence with the computer simulation.

For static luminescence quenching kinetics in unbounded media there exists a well known non-exponential Forster decay law, which describes the quenching as root time dependence [1–4] (square-root for three-dimensional case and dipole–dipole interaction).

Nowadays, luminescent nanoparticles are widely used as markers giving rise to the question how the luminescence properties will change depending on the restricted geometry of the material, for example, polymer coils in solutions [5], photonic crystals [6], porous glasses [7,8], nanoparticles [9]. For different donor positions, the configurations of the surrounding acceptors are different and can be controlled via luminescence kinetics. Moreover, restrictions on the possible acceptors positions can lead to diminishing of the space dimension, to, generally, non-integer one. It is not something exotic and can easily be encountered in experiment. For example, if we consider energy transfer when both donors and acceptors can only be located on the surface of spherical nanoparticles, the problem is two-dimensional one, see Ref. [10].

In Refs. [8,9], specifically, luminescence quenching kinetics of donors located on the surface of spherical nanoparticles by acceptors randomly located in the volume has been considered.

Obviously, more general (and, surely, more complicated) case is quenching of donors, which are also randomly located in the nanoparticles volume. We have started the study considering spherical nanoparticles, see recent publication [11]. Here we present the general theoretical solution for the three- (spheres) and two- (circles) dimensional nanoparticles, for cylindrical nanoparticles; and show the results of computer simulation.

In our consideration we let acceptor concentration be small and statistically uniform in the space of nanoparticles. Donor's concentration is much smaller still, so that we can neglect donor-to-donor excitation migration. While computer simulating the experiment, we have put one excited donor in one particle, at random position. Number of acceptors in one particle has Gaussian distribution around the average (number of positions available multiplied by concentration). The concentration is the probability of a certain position to be occupied by an acceptor atom.

The probability of elementary act of energy transfer from a donor to a certain acceptor, located at distance r from a donor, is C_{DA}/r^S, where S – multipolarity of interaction ($S=6$ for dipole–dipole, 8 for dipole–quadrupole, 10 for quadrupole–quadrupole interaction) and C_{DA} – microparameter of energy transfer efficiency.

Let all the nanoparticles be of one size with radius R. First, we will write the expression with the respect to donors located at the certain distance r_D from the center of nanoparticle, and then we will average it over all r_D, $0<=r_D<=R$.

We will give some details on the derivation of the results having in mind two-dimensional case ($d=2$), which is somewhat more difficult than three-dimensional case ($d=3$), which we have addressed in Ref. [11], because it calls for more approximations.

We will start with the same approach as in Ref. [11].

Classically, intensity of luminescence is given by

$$I(r_D,t)=\exp\{-f(r_D)\}, \quad (1)$$

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where the function in the exponent in the continuous approximation has the form

$$f(r_D)=N_A\int_S dS\left(1-\exp\left[-\frac{C_{DA}t}{r^S}\right]\right), \tag{2}$$

where $N_A=cN$ – average number of acceptors in the unit of area (space), N – number of positions available for acceptors in the unit of space, c – fraction of positions occupied (concentration).

We will neglect the size of donor and acceptor atoms (the minimal distance of energy transfer). Therefore, in Eq. (2) we have to integrate either over a whole circle $dS=2\pi r dr$, if $r+r_D<=R$, i.e. $0<=r<=R-r_D$, or over a segment

$dS=dr\,2r\arccos\left(\frac{r_D^2+r^2-R^2}{2rr_D}\right)$ if $r+r_D=>R$ and $r-r_D<=R$ ($R-r_D<=r<=R+r_D$).

$$\begin{aligned}f(r_D)&=N_A\int_0^{R-r_D}dr\,2\pi r\left(1-\exp\left[-\frac{C_{DA}t}{r^S}\right]\right)\\&\quad+N_A\int_{R-r_D}^{R+r_D}dr\,2r\arccos\left(\frac{r_D^2+r^2-R^2}{2rr_D}\right)\left(1-\exp\left[-\frac{C_{DA}t}{r^S}\right]\right)\\&=J_1(r_D)+J_2(r_D)\end{aligned} \tag{3}$$

First integral

$$J_1(r_D)=N_A\int_0^{R-r_D}dr\,2\pi r\left(1-\exp\left[-\frac{C_{DA}t}{r^S}\right]\right) \tag{4}$$

is analogue to the one appearing in consideration of quenching in bulk, but with the bounded upper limit $(R-r_D)$. Here, difference from quenching in bulk comes down to using incomplete gamma-function instead of regular one. When the limit is not small, or for the times t, satisfying

$$1\ll C_{DA}t\ll(R-r_D)^S,$$

we have classic expression [3,4]:

$$J_1\approx N_A\Gamma(1-d/S)(C_{DA}t)^{d/S}\pi\equiv(W_1t)^{d/S}, \tag{5}$$

$$W_1=C_{DA}\left[N_A\pi\Gamma(1-d/S)\right]^{S/d},\quad\text{when } d=2 \tag{6a}$$

$$W_1=C_{DA}\left[N_A4\pi/3\Gamma(1-d/S)\right]^{S/d},\quad\text{when } d=3. \tag{6b}$$

Here the rate W_1—value, inverse to the time when luminescence due to quenching in bulk will decrease by e times.

Second integral

$$J_2(r_D)=N_A\int_{R-r_D}^{R+r_D}dr\,2r\arccos\left(\frac{r_D^2+r^2-R^2}{2rr_D}\right)\left(1-\exp\left[-\frac{C_{DA}t}{r^S}\right]\right) \tag{7}$$

reflects the specifics of the acceptors configuration around near-surface donors—the fact that acceptors are absent in the half (or greater) part of the space around near-surface donors.

Expression (7) with arccosine in it, moreover, its derivate with respect to r, are not easy to integrate, leading us to expand both expressions into a series.

To find the solution, we have used piecewise linear approximation $f(r_D)=h_1(r_D)+h_2(r_D)$, where h_1 coincides with the horizontal part of J_1 up to a point R_x of intersection of the horizontal line and tangent line to J_2 in the point $r_D=R$ (here, value of $-f(R)=-J_2(R)$ has the maximum, tangent values are also the same $f'(R)=J'_2(R)$). After $r_D=R_x$ h_1 is identically zero, while h_2, alternatively, is zero at $r_D<R_x$, and for $r_D\geq R_x$ $h_2(r_D)=J_2(r_D=R)-(R-r_D)J'_2(r_D=R)$ linearly approximates J_2.

In the final point $r_D=R$, $f(r_D)$ value is approximately twice smaller than the value in the starting point $r_D=0$:

$$J_2\big|_{r_D=R}=\frac{(W_1t)^{d/S}}{2}\left(1-2k_0\frac{(W_1t)^{1/S}}{N_{AP}^{1/d}}\right). \tag{8}$$

Here we introduce parameter N_{AP}—average number of acceptors in one nanoparticle:

$$N_{AP}=\pi R^2N_A,\quad\text{for } d=2, \tag{9a}$$

$$N_{AP}=\frac{4}{3}\pi R^3N_A,\quad\text{for } d=3, \tag{9b}$$

and parameters

$$k_0=\frac{2\Gamma(1-3/S)}{3\pi\left[\Gamma(1-2/S)\right]^{3/2}}\approx0.2\quad\text{and}$$

$$k_1=\frac{2\Gamma(1-1/S)}{\pi\left[\Gamma(1-3/S)\right]^{1/2}}\approx0.6\quad\text{for the case of dimension } d=2, \tag{10a}$$

$$k_0=\frac{3}{16}\frac{\Gamma(1-4/S)}{\left[\Gamma(1-3/S)\right]^{4/3}}\approx0.2,$$

$$k_1=\frac{3}{4}\frac{\Gamma(1-2/S)}{\left[\Gamma(1-3/S)\right]^{2/3}}\approx0.7\text{ for the three-dimensional case.} \tag{10b}$$

Tangent to the function $-f(r_D)$ has a form

$$q=-J'_2\big|_{r_D=R}=\frac{(W_1t)^{d/S}}{R}\left(\frac{k_1N_{AP}^{1/d}}{(W_1t)^{1/S}}-k_0\frac{9(W_1t)^{1/S}}{8N_{AP}^{1/d}}\right)$$

for the two-dimensional case, (11a)

$$q=\frac{(W_1t)^{3/S}}{R}\left(\frac{k_1N_{AP}^{1/3}}{(W_1t)^{1/S}}-k_0\frac{(W_1t)^{1/S}}{N_{AP}^{1/3}}\right)$$

for the three-dimensional case. (11b)

Crossing point of horizontal line and tangent line in $r_D=R$ is time-dependent $R_x(t)$: $R_x=R(1-\Delta R)$, where $\Delta R=(W_1t)^{1/S}/(2k_1N_{AP}^{1/d})$.

The result for quenching kinetics is

$$I=\left(1-\frac{(W_1t)^{1/S}}{2k_1N_{AP}^{1/d}}\right)^d e^{-(W_1t)^{d/S}}+z(W_1t)e^{-(((W_1t)^{d/S})/2)\left(1-2k_0(((W_1t)^{1/S})/(N_{AP}^{1/d}))\right)}, \tag{12}$$

where

$$z=2\frac{(-1+qR)+\exp(-qR\Delta R)\{1-qR_x\}}{(qR)^2}\quad\text{for } d=2, \tag{13a}$$

$$z=\frac{3}{(qR)^3}\left(2-2qR+q^2R^2+\exp(-qR\Delta R)\left\{-2+2qR_x-q^2R_x^2\right\}\right)\quad\text{for } d=3. \tag{13b}$$

The formula for z (13) must be taken into account when considering kinetics at time $(W_1t)^{d/S}<1$. When one is interested in kinetics at longer stages ($(W_1t)^{d/S}>1$), it can be considerably simplified, however, only under the condition that $(W_1t)^{d/S}$ is smaller than average number of acceptors in one nanoparticle N_{AP}, (see Eq. (11)):

$$I=\left(1-\frac{(W_1t)^{1/S}}{2k_1N_{AP}^{1/d}}\right)^d e^{-(W_1t)^{d/S}}+\frac{d}{k_1N_{AP}^{1/d}(W_1t)^{(d-1)/S}}e^{-\frac{(W_1t)^{d/S}}{2}\left(1-2k_0\frac{(W_1t)^{1/S}}{N_{AP}^{1/d}}\right)},$$