

Modeling Exciton Diffusion in Nanoparticles

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Overview

First, let's get some terms out of the way. By *exciton*, here we are referring to a localized molecular excitation on a relatively short segment of conjugated polymer. This type of molecular exciton is very different from typical (Wannier) excitons in inorganic semiconductors (which are considered electron-hole pairs and are much larger, are much more weakly bound, and are typically only stable at very low temperatures, 4 K or less). Heeger (Nobel prize-winner) has theorized that conjugated polymers are very much like inorganic semiconductors, and that excitons in CP's are also weakly-bound electron-hole pairs. However, there is considerable evidence that this view is wrong, and he is in the minority on this subject. The type of exciton we are referring to for conjugated polymers is the small or *molecular exciton* (sometimes called a Frenkel exciton, but I prefer not to, see below), which consists of a molecule in the π^* excited state and the polarization of the surrounding polymer molecules. Strong coupling between the transition dipoles of nearby chromophores can give rise to collective excitations called *Frenkel excitons*, which can in principle be many times larger than a single chromophore. Frenkel excitons often exhibit an energy shift or energy splitting, referred to as the Davydov splitting. However, for the sake of simplicity, here we will assume that the excitons are small—much smaller than the nanoparticle, and we will assume that Frenkel exciton behavior (such as collective excitation, Davydov splitting and coherent, ultrafast energy transfer) is either unimportant or is partially taken into account in the exciton diffusion theory, *i.e.*, ultrafast/coherent transport results in a somewhat larger exciton diffusion length.

Another quick note about excitons. Wikipedia, and many other places, define an exciton as a bound state of an electron and hole which are attracted to each other by a Coulomb force. While this is correct for Wannier excitons, it is **very wrong for molecular/Frenkel excitons**, since the picture of a bound electron-hole pair typically doesn't make sense for molecules. For example, if we plug in a typical molecular exciton binding energy of 0.5 eV and a typical dielectric constant of 4, this gives an orbit of less than 1 Å, much smaller than the molecule. This is physically absurd, thus the electron-hole pair picture doesn't make sense for molecular/Frenkel excitons. Additional information about Frenkel excitons and the Frenkel-exciton Hamiltonian, which is based on coupling of transition dipoles, is given in a paper by Kasha and El-Bayoumi, "The Exciton Model in Molecular Spectroscopy."

By *chromophore*, I am referring to a small segment of the polymer chain, typically 3-8 polymer repeat units in length. The exciton can “hop” more or less randomly from chromophore to chromophore repeatedly during the lifetime of the exciton. Because of the similarity of this behavior to the phenomenon of diffusion, this process is called *exciton diffusion*, and it occurs by either overlap of molecular orbital wavefunctions (often referred to as Dexter transfer), by Förster transfer, or by coherent ultrafast energy transfer. All are known to occur, likely simultaneously, and it can be difficult to experimentally determine which process or processes are dominant. The question of which mechanism dominates depends on a variety of system physical parameters such as chain conformation, disorder, interchromophore distances, transition dipole moments, temperature, and the electronic states (molecular orbitals) involved. We might want to design some experiments (low T experiments, maybe some time-resolved polarization anisotropy) to investigate these issues, including such basic issues as effective chromophore size and the length scales and time scales of individual hopping events, but for now, in this document, we will not worry further about the detailed mechanism for exciton hopping/diffusion.

In the standard picture of exciton diffusion theory, at any given moment in time, an exciton can either hop to another site (diffuse), decay radiatively (emit a photon), or decay non-radiatively (there are many possibly non-radiative pathways, including internal conversion to vibrations, electron transfer to make a charge-separated state, or intersystem crossing to make a triplet state). In a disordered material there are additional complications, because there will be a range of chromophore energies, and exciton hopping will tend to proceed from higher energy chromophores (ones with a larger π - π^* gap) to lower energy chromophores, eventually becoming trapped at low-energy chromophores. This tends to result in the relatively large gap between excitation and emission (as compared to dyes) typically seen for conjugated polymers, particularly for the films and nanoparticles, and other phenomena, such as a progressive red-shifting of the emission on the few picosecond timescale (seen in fluorescence upconversion experiments) and a related slowing-down of the rate of the energy diffusion on the picosecond timescale, as the typical exciton energy decreases and the fraction of energetically accessible chromophores decreases—as an exciton gets redder, there are fewer and chromophores that are still redder and can thus accept the exciton. We will also ignore these phenomena in our model, for now, but it is worthwhile to note them.

If we add an energy acceptor (dye/quencher), then occasionally an exciton will decay by transferring its energy to the acceptor, likely via a Förster transfer (FRET) mechanism. Since the rate of FRET depends on the inverse sixth power of the distance, and the dyes and excitons are distributed more or less randomly, this gives rise to a large range of energy transfer rates. This process has been examined in some detail for a number of years, dating back to early work in the 60’s and 70’s by Powell (look in the EndNote database) on doped anthracene crystals, and more recently by theorists such as Nakanishi and experimentalists such as Andy Monkman. Many details haven’t been figured out, and it’s still not clear the relative roles of exciton (chromophore) size, Dexter vs. Förster transfer, collective excitations (coherent energy transfer, Frenkel exciton picture), energetic disorder, etc.

The conjugated polymer nanoparticles give us another window into these energy transfer

phenomena. By controlling the particle size, we can control the length scale over which energy transfer occurs. We also have some control of polymer phase (e.g., the beta phase in PFO). Also, it is much easier to collect accurate and reproducible fluorescence quantum yield results and time-resolved fluorescence (TCSPC) on the nanoparticle dispersions than it is to collect data on thin films. Most prior work in this area is on thin films. Thin films tend to be difficult to reproduce, and there are interface effects and waveguiding effects that are hard to quantify, control and model.

We have already seen some evidence that energy transfer efficiency depends on particle size. This is exciting, and provides the motivation to study these effects further. We plan on conducting a number of TCSPC studies to look at energy transfer for a range of particle sizes and doping concentrations. By careful analysis of the TCSPC traces, we hope to find direct evidence of “distributed” energy transfer rates (a range of rates due to the random distribution of dyes and range of Forster distances). This by itself should be publishable in a P-Chem journal. In addition, we could follow this up with time-resolved polarization anisotropy (straight-forward, just add polarizers to the TCSPC setup), single molecule measurements, and low temperature measurements. We could even later add femtosecond time-resolved fluorescence upconversion measurements (if you’re interested, I could point you to some papers on how this is done). All of these results should give us an unprecedented level of detail in determining the fundamental physics of exciton interactions and energy transfer in CPs and other molecular semiconductors. This is a very important practical and fundamental question, very relevant to optimizing our nanoparticles for PDT and other applications, and even for other applications such as polymer displays and solar cells.

We are way ahead of the competition in that we already have flexible, sophisticated, easy-to-use code for an exciton diffusion and energy transfer model that works for nanoparticles (trivial to extend to bulk films—just use larger nanoparticles), and we have the nanoparticle system and fluorescence quantum yield and lifetime data. This should lead to a series of publications in physical chemistry journals and possibly high profile publications as we progress.

3D Random Walk Model: Monte Carlo Approach

We are modeling the combined processes of exciton diffusion, fluorescence, non-radiative relaxation, and energy transfer using a 3D random walk simulation employing a Monte Carlo approach—simulating random exciton trajectories using a random number generator. Previously, in Changfeng’s dye-doped nanoparticle paper and papers by Jiangbo, we treated the motion of the excitons as a random walk on a 3D cubic lattice. There were some shortcomings with that code when it came to simulating our recent (2012) experiments, so I started writing a different version, and in the process found a bug in the old code that is difficult to fix (and introduces some error, but not enough to invalidate our previous results). Therefore we are switching to the new code, based on a slightly different picture of diffusion and Brownian motion. I have verified that this code is more accurate than the previous code, and it has been extensively tested. Here is the approach taken for the new code. According to Brownian motion theory, if we have a particle with a diffusion coefficient D , initially at position x_0 at time

t_0 , the particle will, at a later time t , be at a random position given by a Gaussian probability distribution,

$$p(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-x_0)^2/2\sigma^2},$$

where the standard deviation σ is given by

$$\sigma = \sqrt{2D(t - t_0)}.$$

It can be shown that trajectories that the above expressions reproduce the correct 1D Brownian motion behavior for the mean square displacement $\langle x^2(t - t') \rangle$,

$$\langle x^2(t - t') \rangle = 2Dt$$

Thus, in our Monte Carlo approach, if we have a time step Δt , we can propagate the particle (exciton) at each time step by generating a Gaussian-distributed random numbers with a standard deviation of σ . In MATLAB this is achieved by the `randn` function—you are encouraged to familiarize yourself with the function. For example, plotting `plot(3*randn([1 100]))` will plot gaussian-distributed random numbers with a standard deviation of 3. We also need to add the possibilities of decay (fluorescence) and energy transfer to our random walk, and we need to calculate the diffusion constant based on the lifetime and diffusion length.

In the exciton diffusion experiments, it is difficult to determine the diffusion constant directly, so usually what is determined and reported in the literature is an exciton *diffusion length*, L_D , typically in the range of about 4 nm to 15 nm for conjugated polymers. Exciton diffusion lengths as high as hundreds of nm are reported for highly crystalline anthracene at low temperature. Be careful when looking in the literature—there are lots of improbably large exciton diffusion lengths reported, likely due to systematic error, sloppy experiments, overinterpreted experiments, etc. For example, Gregg et al. concluded that thin films of a perylene derivative (PPEI) yielded large (2.5 μm !) exciton diffusion lengths, on the basis of experiments in which a film was excited from one side and the emission of an acceptor layer on the other side of the film was measured (B. Gregg 1997 JPC-B). However, disorder (pinholes, etc) in the PPEI film, intermixing of the layers, and perhaps some waveguiding were likely responsible for the observed acceptor emission—other experiments with uniformly dye-doped films and using NSOM were unable to reproduce the large exciton diffusion lengths previously reported (J. McNeill, 2000 JCP). Be suspicious if anybody reports anything above 15 nm for a conjugated polymer or disordered material (such as 2010-2011 Barbara papers, older papers by Gregg, Buratto, etc). The relationship between diffusion length L_D , the diffusion constant D , and donor lifetime τ_d is defined by,

$$L_D = \sqrt{2D\tau_d},$$

which can be easily rearranged to give D from the experimentally-determined L_D and τ_d .

Typically the parameters we plug into a simulation are the diffusion length L_D , the Förster radius R_0 , the particle size, the pure donor fluorescence lifetime τ_d , particle size R_{np} and the time step Δt , typically set to be at least a factor of 20-50 smaller than the lifetime of the donor. The basic physical picture then is that we have an exciton that is generated at some

random position within a nanoparticle. The exciton hops from site to site within the sphere of the nanoparticle over many time steps, and at each time step it can undergo decay or energy transfer. The exciton continues on its trajectory until decay or energy transfer occurs.

Now let's get down to the problem of calculating trajectories. At each time step, there is some probability that the exciton will decay by either fluorescing or undergoing energy transfer. We need an expression for calculating the probability of fluorescence decay per time step. The probability of a given exciton decaying per time step is given by,

$$p = 1 - e^{-\Delta t/\tau_d} \simeq \frac{\Delta t}{\tau_d}.$$

So, at each time step (each iteration in a loop), we generate a random number between 0 and 1, and compare it to the above probability to determine if the exciton decays.

Now we need an expression for the probability of FRET occurring during a given timestep. We know that the rate of energy transfer k_{ET} is given by the expression,

$$k_{ET} = \frac{1}{\tau_D} \left(\frac{R_0}{R} \right)^6$$

Thus the probability of energy transfer at a given time step is given by,

$$p_{ET} = \frac{\Delta t}{\tau_D} \left(\frac{R_0}{R} \right)^6$$

Since there will typically be multiple acceptors in a nanoparticle, in our simulation we will need to sum up the rates of energy transfer of a given exciton to each acceptor to give a total energy transfer rate.

The structure of the `etdiffnp` simulation code

In order to properly simulate this exciton hopping process using a Monte Carlo approach, we need to run lots and lots of randomly generated trajectories and collect information about what occurred and when for each exciton trajectory. In addition, we will average over many possible random arrangements of dye molecules, since the arrangement of dye molecules will vary from particle to particle and that will affect the results. There are 3 MATLAB scripts that do the work: `etdiffnp.m`, `etdiffnp_hlp.m`, and `etdiffnp_fun.m`.

`etdiffnp.m` is the script that sets up the system physical parameters and simulation parameters, runs the other scripts that do the actual simulations, and saves and plots the simulation results. This is the script that you will have to edit.

`etdiffnp_hlp` is the script that does some additional setup (mostly generating the random dye positions) and calls `etdiffnp_fun`, which calculates the exciton trajectories by a 3D random walk.

To run the simulations, edit `etdiffnp.m` and change parameters to match the parameters for the system you want to simulate. You'll probably want to put the simulation scripts in a directory like `c:\diffmodel`. Then start MATLAB, type `cd c:\diffmodel` and then run

`etdiffnp`. After about 5-10 minutes, the simulation should end, and the donor fluorescence lifetime simulation results will be plotted. The time variable is `tt`, the fluorescence intensity is in `fdecay`, and the energy transfer efficiency is in `EffVec`. Several useful numbers are also printed to the command window, including the quenching efficiency, its uncertainty, and the mean exciton lifetime. I will try to add a fit to find the β parameter, as well.

Notes on simulations of non-exponential dynamics

These are miscellaneous notes regarding the simulations. We will discuss these after you've digested this document and taken a look at the code and run a couple of simple simulations.

1. We need to increase the number of excitons, `nex` in order to get reliable lifetime information. Keep increasing `nex` and/or `navg` until `length(decaylist)` is above 20000. Maybe closer to 100,000 will be required to get the noise level down to a level where we can get acceptable fits to find the stretch parameter. We can also edit the `histran` variable to make the bin sizes larger for the histograms, but this also worsens the time resolution.
2. Will want to get good lifetime simulations for energy transfer efficiencies ranging from about 20% to about 80%.
3. If 1 quencher per particle gives a quenching efficiency that is higher than you need (say, you want 20% but it gives 40%), then increase the particle size, or decrease the Forster radius or diffusion length, depending on what makes more sense. If you are not sure, then just increase the particle size.
4. Once we get the decays, we will want to fit them to a "stretched exponential" (actually Wikipedia has a nice intro on this function) in order to try to determine the "stretch" parameter β , and how the average lifetime and the stretch parameter are related to the average energy transfer efficiency.
5. I'm not sure if the code has the right particle size, diffusion length, particle radius that correspond to the PFBT nanoparticles you have been making. Hopefully you can obtain the correct numbers from JJ's dissertation or Jiangbo's paper (run them by me as well).
6. The amount of time it takes to do a simulation is very sensitive to `dt`. It might be best to start with a relatively large `dt` like 10 or 20 ps, and a small `nex=1500`, try a bunch of different `ndye` values until you get efficiency that is about right, then once you have found the right `ndye`, reduce `dt` to 5, 2 or even 1 ps, to improve accuracy and time resolution at a cost of increased simulation time), and also crank up `nex` and `navg` to make the decays less noisy. In other words, a larger time step and fewer excitons or averages gets you fairly accurate efficiency results fast, so you can figure out how many quenchers you want to use. After that, for more accurate dynamics, you need to increase the number of excitons and averages, and reduce the time step.

7. Be careful not to confuse radius with diameter. It's an easy mistake to make.
8. You might want to first do some semilog plots and check for deviations from exponential behavior.
9. I have some fitting code called `theofit`. To use it on some simulation results, change to the appropriate directory and run `theofitrn`. The parameters are τ_{kww} and β , respectively. τ_{kww} is usually a number between 20 and 300 (picoseconds), and the stretch parameter β should be a number between 0.3 and 1.
10. Further down the to-do list is to try to estimate what the acceptor dynamics should look like. There should be an exponential or stretched exponential rise. We should work through the appropriate rate equations for the simple case and also simulate what the data would look like, to see if we have a chance of possibly getting out some useful information from TCSPC measurements of the rise of the acceptor emission.

Append A - Energy Transfer Efficiency as a Function of Distance

For checking the code, I verified that, in the absence of diffusion, energy transfer to a single quencher gives the proper curve for energy transfer efficiency (probability) as a function of distance R . The proper functional form is,

$$p(R) = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6}$$

Appendix B - Diffusion and Decay With a Point Source/Sink

For checking the code, I verified that it reproduces the correct behavior for a pointlike sink (a quencher with R_0 set to 0.1 nm, $L_D = 3$ nm). The functional form for diffusion and decay from a point source is identical to (or a mirror image of) the functional form for diffusion and decay for a point sink. This problem was perhaps first solved by Fermi in his calculations of neutron diffusion leading up to the demonstration of the first nuclear fission chain reaction, and comes up in a number of real world problems, such as spreading of a radioactive plume, spreading of toxic compounds in an aquifer, etc. At steady-state, diffusion-decay from a point source in 3D yields a density of,

$$n(R) = \frac{n_0 K_0 (R/L_D)}{R}$$

where K_0 is the zeroth-order modified Bessel function and n_0 is the density at the point source. In MATLAB, this is given by `besselk(0, R/LD)`. In 2D, the solution is,

$$n(R) = \frac{n_0 K_0(R/L_D)}{\sqrt{R}},$$

and in 1D, the solution is,

$$n(x) = n_0 K_0(x/L_D).$$

For diffusion-related information, I suggest a web search and literature search on the key words “diffusion length”, the Powell papers, and the book *The Mathematics of Diffusion*, by J. Crank.