

# Monte Carlo Modelling of Exciton Diffusion in Polyfluorenes

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In a conjugated polymer solar cell, the absorption of solar photons produces temporary electrical excitations (excitons) which may exist for up to 1 ns before recombining. For an efficient cell, as many excitons as possible must migrate to dissociation regions, such that they form free electron hole pairs rather than recombining. (Dissociation typically occurs at an interface between hole and electron conducting polymers.) A highly efficient example of controlled exciton transport is the funnelling of energy to reaction centres by antenna systems in natural photosynthesis. To mimic this efficiency in synthetic devices, a detailed understanding of exciton transport within conducting polymers is necessary.

To date, numerical models of exciton diffusion have employed some crude assumptions. For instance, the chromophores (polymer chain segments) between which excitons hop are assumed to be arranged on a cubic lattice. Also, the rate of hopping between one chromophore and another is typically calculated assuming the Förster mechanism where energy transfer is taken to occur as a result of electronic coupling between two point dipoles (the donor and acceptor chromophores). This method of calculating hopping rates is only valid when the separation between the two chromophores is large compared to their lengths, which is not usually the case in conjugated polymers. Even with these assumptions, reasonable quantitative agreement with experiment has been achieved [1]. However, a more realistic model may provide insight into details of exciton transport which are pertinent to efficient solar cell device design.

In our model, an aggregate of polymer chains is described at the level of carbon atom coordinates. Polymer chains, and their constituent chromophores, are assigned lengths based upon distributions determined by experiment. Chains are arranged on a hexagonal lattice, but have some perturbation from regular alignment. Random translations are made along the direction parallel to the chain axes. On any given chain, torsional angles exist between one chromophore and the next. In this way we hope to approximate some of the spacial disorder present in a real conjugated polymer. Calculations are currently for polyfluorenes, which experiments suggest have fairly regularly packed, rod like chains.

The exciton hopping rates between one chromophore and another are calculated by our collaborators at the University of Mons Hainaut, Belgium. They use quantum chemical methods which give an improved representation of energy transfer between chromophores. Instead of treating chromophores as point dipoles, the new method uses the distributed monopole model, which takes into account the spacial shape of the donor and acceptor chromophores when calculating their electronic coupling. The electronic couplings are used in conjunction with Fermi's golden rule to calculate hopping rates. Findings of the method compare well with those of ultrafast spectroscopy experiments [2]. A principal result is that inter-chain hops are typically faster than intra-chain hops.

Our collaborators at Mons calculate hopping rates from each chromophore to its neighbour chromophores. Given these, and the description of the morphology, it is possible to do a dynamical Monte Carlo simulation of exciton transport, as for instance used by Meskers et. al. [1]. An example exciton trajectory is shown in figure 1. Averaging over a large number of Monte Carlo trials, transport properties such as diffusion length and the spacial dependence of recombination probability (figure 2) can be calculated. As shown in figure 2, motion in the direction parallel to the polymer chains is

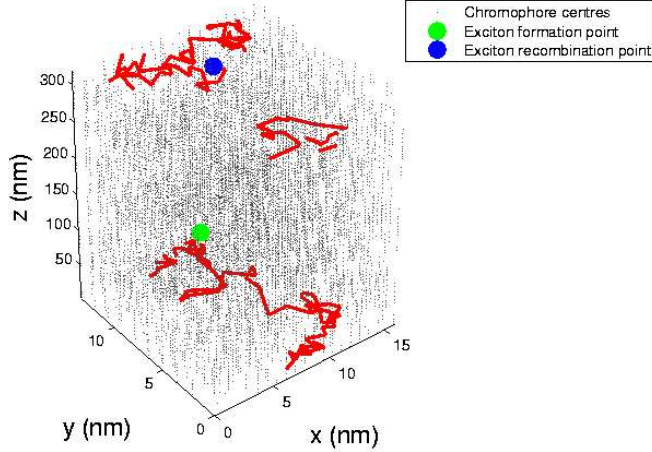


Figure 1: An example of an exciton trajectory generated by the dynamical Monte Carlo algorithm.

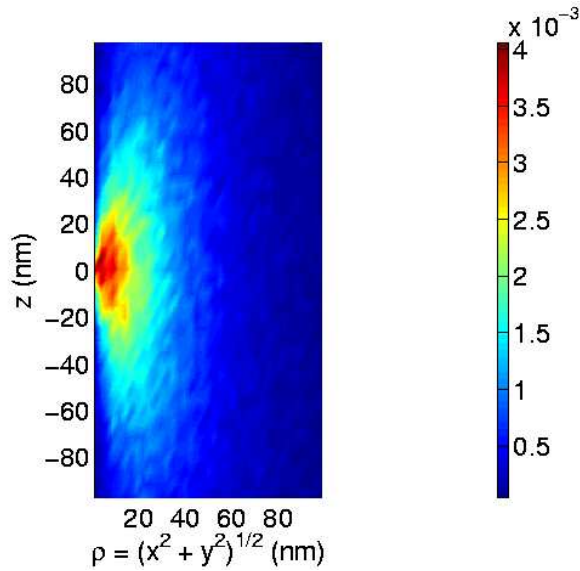


Figure 2: Exciton recombination probability as a function of position relative to the point of exciton creation.  $z$  is the direction parallel to the chains, and  $\rho$  is the radial distance perpendicular to the chains.

more likely than motion in perpendicular direction, despite inter-chain hops being faster. This result is explained as follows: (1) while intra-chain hops are slower, and therefore less common, they involve large distances relative to inter-chain hops; and (2) inter-chain hops actually involve a large component in the direction parallel to chains.

## References

- [1] S. C. Meskers, J. Hübner, M. Oestreich, and H. Bässler. Dispersive relaxation dynamics of photoexcitations in a polyfluorene film involving energy transfer: experiment and monte carlo simulations. *Journal of Physical Chemistry B*, 105:9139–9149, 2001.
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