The effects of orientational and energetic disorder on Forster energy migration along a one-dimensional lattice

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Abstract

Numerical simulations of exciton migration along a one-dimensional lattice via Forster energy transfer are reported. The roles of static Gaussian energetic disorder and transition dipole orientational disorder are investigated. Both disorder mechanisms result in subdiffusive behavior during the initial phase of energy migration, tending asymptotically to normal diffusion. The dependence of the subdiffusion parameters on the inhomogeneous linewidth and intersite spacing is examined. Depending on the exciton lifetime, subdiffusive motion may dominate the exciton displacement behavior, and it becomes problematic to use normal diffusion theory to make even qualitative predictions about the exciton motion.

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1. Introduction

In many of these applications of conjugated organic materials, the phenomenon of electronic energy transfer (EET) plays an important role. In a solar cell, rapid exciton diffusion is desirable, since it increases the probability that a photoexcitation will encounter a charge-separation site and produce photocurrent [1]. For many conjugated polymer sensors, the ‘amplification’ effect that leads to their high sensitivity to quenching analytes relies on EET as well [2–4]. Central to both applications of organic materials is the magnitude of the exciton diffusion length

$$L_D = \frac{D R_0^3}{\lambda}$$

where $D$ is the diffusion constant and $\lambda$ is the exciton lifetime. Nondiffusive exciton motion can degrade the performance of such devices, as recently suggested for the generation of photosensitized charge carriers in conjugated polymers [5]. Because exciton motion is critical for technological applications of conjugated organic molecules, it is vital to understand how it is affected by the chemical characteristics of specific systems.

For incoherent exciton motion in dense chromophore systems, the dipole-dipole interaction is usually assumed to be dominant, leading to the Forster EET mechanism [6]. Forster’s original paper on EET derived an expression for the exciton diffusion constant in several different types of three-dimensional lattices [7]. In general, the diffusion coefficient $D$ is related to the molecular properties via [8].

$$D = B \frac{R_0^6 / \lambda^{4/3}}{\tau_{\text{rad}}}$$

where $B$ is a constant on the order of unity, $\rho$ is the number density, and $\tau_{\text{rad}}$ is the radiative lifetime. $R_0$ is the Forster radius, defined by

$$R_0^6 = \frac{9000 \ln(10) \phi \kappa^2}{128 \pi^2 N_A \lambda^4} \int_0^\infty \bar{\alpha}(\nu) f(\nu) \frac{d\nu}{\nu^4}$$

$$\frac{1}{\tau_{\text{FRET}}} = \frac{1}{\tau_0} \frac{R_0^6}{R^6}$$

where $\alpha$ is the index of refraction, $\phi$ is the quantum yield, $\kappa^2$ is an orientation factor, $N_A$ is Avogadro’s number, $\bar{\alpha}(\nu)$ is the absorption spectrum and $f(\nu)$ is the fluorescence spectrum whose integral has been normalized to 1. The Forster resonance energy transfer time, $\tau_{\text{FRET}}$, depends on $R_0$ as...
as well as $R$, the interchromophore distance, and the fluorescence lifetime $\tau_B$. Eqs. (1) and (2) provide a simple way to predict exciton diffusion behavior based on the spectral properties and concentration of the chromophores. The validity of these equations for real chemical systems is suspect, however. For example, simple diffusive behavior is generally not observed when the spatial distribution of chromophores is random [9–13]. The effect of energetic disorder has also been explored in specific chemical systems [14–22], usually in the context of a specific experimental observable like fluorescence anisotropy or spectral shifting.

In the present work, we use numerical simulations to directly observe the spatial displacement of the exciton and determine when the motion becomes subdiffusive. To this end, we study the EET dynamics of a simple model system: a one-dimensional chain of chromophores interacting via the Förster mechanism. By varying the degree of static disorder, both energetic and orientational, we examine how these two factors affect the diffusive motion of the exciton.

Our work complements early work by Katsuura on the Förster migration of excitations on a one-dimensional random lattice [23], and more extensive work by Bassler et al. on exciton diffusion by activated hopping [24]. We find that as the amount of orientational or energetic disorder is increased, the simple diffusive motion predicted by Eq. (1) gives way to subdiffusive motion tending asymptotically toward a much slower diffusion. The dependence of the subdiffusion rate on molecular parameters like the fluorescence Stokes shift, the intermolecular spacing, and the homogeneous and inhomogeneous linewidths is investigated. Our results suggest that disorder-induced subdiffusion may be an important limiting factor for exciton diffusion lengths in amorphous conjugated polymers and oligomer solids.

2. Methods

We consider energy transfer along a one-dimensional chain of molecules as outlined in Fig. 1, which contains all the physical effects we expect to be important for linear polymer systems [25–28]. The intersite distance $R$ is fixed, but the site energies and dipole orientations are allowed to vary. The model chromophore is equivalent to a three-level system and gives rise to different absorption and fluorescence frequencies due to the fluorescence Stokes shift. The absorption and fluorescence lineshapes, subject to the same amount of Gaussian homogeneous broadening, are given by:

\[
\text{Abs}(v) = \varepsilon_{\text{peak}} \exp \left[ -\frac{(v_A - v)^2}{\sigma_h^2} \right] \quad (3)
\]

\[
\text{Fl}(v) = \frac{1}{\sigma_h \sqrt{2\pi}} \exp \left[ -\frac{(v_A - v - \Delta_{SS})^2}{\sigma_h^2} \right] \quad (4)
\]

where $\sigma_h$ is the homogeneous $1/e$ width of the absorption line, $v_A$ is the absorption frequency and $\Delta_{SS}$ is the Stokes shift of the fluorescence. All frequency units are in cm$^{-1}$. $\varepsilon_{\text{peak}}$ is the peak absorption coefficient of the absorption lineshape, in units of M$^{-1}$ cm$^{-1}$. In addition to the homogeneous broadening, the heterogeneity of the local environments of the absorbers is assumed to lead to a Gaussian distribution of absorption energies, with a variance $\sigma_i$:

\[
\text{Inhom}(v) = \frac{1}{\sigma_i \sqrt{2\pi}} \exp \left[ -\frac{(v_A - v)^2}{2\sigma_i^2} \right] \quad (5)
\]

In order to determine the Förster radius $R_0$, we evaluate the spectral overlap integral given by

\[
\text{Ovlp} = \int_{-\infty}^{\infty} \text{Abs}(v) : \text{Fl}(v) \frac{dv}{v^4} \quad (6)
\]

For the Gaussian lineshapes assumed in this work, the spectral overlap integral for two chromophores, absorbing at frequencies $v_A$ (donor) and $v_B$ (acceptor) respectively, is given by

\[
\text{Ovlp}(A \rightarrow B) = \frac{\varepsilon_{\text{peak}}}{\sqrt{2}} \frac{1}{\left( \frac{1}{2} (v_A + v_B + \Delta_{SS}) \right)^4} \exp \left[ -\frac{1}{2\sigma_h^2} (v_A - v_B - \Delta_{SS})^2 \right] \quad (7)
\]

where we have assumed that the $v^4$ term does not vary significantly over the lineshape. In this case, the Förster radius for energy transfer from chromophore A to B is given by

\[
R_0^2(A \rightarrow B) = 8.82 \times 10^{-22} \frac{\phi_B \kappa^2}{\mu^4} \frac{\varepsilon_{\text{peak}}}{\sqrt{2}} \frac{1}{\left( \frac{1}{2} (v_A + v_B + \Delta_{SS}) \right)^4} \exp \left[ -\frac{1}{2\sigma_h^2} (v_A - v_B - \Delta_{SS})^2 \right] \quad (8)
\]

If we calculate the rate of $A \rightarrow B$ transfer and the rate of $B \rightarrow A$ transfer, the ratio of the rates is the ratio of the spectral overlaps, and we find that
\[
\frac{k_{\text{B}}}{k_{\text{A}}} = \exp \left[ \frac{-2\Delta_{\text{SS}}}{\sigma_h^2} (\nu_B - \nu_A) \right]
\] (9)

In the theory of line broadening due to low-frequency phonons, \(\sigma_h\) is temperature-dependent [29]:
\[
\sigma_h^2 = \sigma_0^2 + 2kT\Delta_{\text{SS}}
\] (10)
and if we assume that the second term is dominant at high temperature, we obtain
\[
\frac{k_{\text{B}}}{k_{\text{A}}} = \exp \left[ \frac{(\nu_B - \nu_A)}{kT} \right]
\] (11)

In this way, our Gaussian lineshape model can fulfill the detailed balance condition in the high temperature limit. Note that we do not consider dynamic disorder in this model [30,31].

We use numerical simulations to look at how the mean square displacement \(\langle x^2 \rangle\) evolves with time. For energetic disorder, the absorption energy of each chromophore is randomly chosen from the Gaussian distribution given in Eq. (5). For orientational disorder, the angles \(\theta_A\) (planar angle between A and B dipoles) \(\theta_B\) (angles of dipoles A and B with respect to intermolecular axis) are chosen randomly, and the orientation factor \(\kappa^2\) is evaluated according to the equation
\[
\kappa = \cos(\theta_A) - 3 \cos(\theta_B) \cos(\theta_A)
\] (12)

A computer program generates a group of chromophores on a \(N = 100\)–\(1000\) site lattice with spacing \(R\). The number of lattice sites is varied, depending on the magnitude of \(\langle x^2 \rangle\). For all the calculations presented in this letter, we used the following parameters: \(\phi_B = 1.0, n = 1.39, \nu_A = 20000\) cm\(^{-1}\), \(\tau_B = 1.0\) ns, \(\sigma_h = 300\) cm\(^{-1}\), \(\nu_{\text{peak}} = 10000\) M\(^{-1}\) cm\(^{-1}\). Together with Eq. (2) these values define a \(N \times N\) matrix of Forster energy transfer rates between all the sites. The temporal evolution of an initial excitation residing on the central chromophore at \(t = 0\) can be found by diagonalizing the matrix and using the resulting eigenvalues to generate the time-dependent displacement [32,33]. This is done for multiple runs for different configurations and the results are averaged together until the \(\langle x^2 \rangle\) curve does not change. Typically, convergence of the results requires on the order of 100 runs. Examination of individual runs showed a continuous distribution of distances traveled, as expected for a random walk process. Fig. 2 shows an example of such a calculation on a 300 site lattice where the population distribution begins as a delta-function on the center site but quickly broadens into a Gaussian distribution. The \(1/e\) half-width of the time-dependent distribution is taken to be \(\langle x^2 \rangle\), the mean square displacement of the exciton in time.

3. Results and discussion

We first examine the role of static orientational disorder on the exciton diffusion rate. In the simplest case, with \(\Delta_{\text{SS}} = 0, \sigma_i = 0, \) and \(\kappa^2 = 2/3\) (this value assumes the reorientation of the dipoles occurs on a timescale faster than the EET). Our numerical simulations recover Forster’s earlier analytical results for the exciton diffusion rate. The mean square displacement \(\langle x^2 \rangle\) increases linearly with time:
\[
\langle x^2 \rangle = 2Dt
\] (13)
From the slope of the line in Fig. 3a we extract a value \(D = 7.6 \times 10^3\) nm\(^2\)/ns = \(7.6 \times 10^{-2}\) cm\(^2\)/s. If we compare this with the expression for \(D\) given by Eq. (1), we find that the constant \(B = 1.09\). It is important to emphasize that setting \(\kappa^2\) to any constant value is equivalent to assuming an ordered system as far as the diffusive dynamics are concerned. If we allow the chromophore angles to vary randomly from 0 to \(2\pi\), the resulting interchromophore angles \(\theta_A\), \(\theta_B\), and \(\theta_{\text{B}}\) lead to a different \(\kappa^2\) factor for each pair of sites. This situation corresponds to a sample with completely uncorrelated orientational disorder. Instead of increasing linearly with time, the \(\langle x^2 \rangle\) curve has a noticeable curvature. A similar effect is observed for increasing \(\sigma_i\), the amount of inhomogeneous broadening, while maintaining \(\kappa^2 = 2/3\), as shown in Fig. 3a too. This subdiffusive behavior leads to a slower increase of \(\langle x^2 \rangle\), as expected for an exciton that sees a distribution of intersite transfer rates [34]. In order to more clearly show the deviation from normal diffusive behavior, we replotted the data in Fig. 3a in terms of log(\(\langle x^2 \rangle\)) versus log(\(t\)). The log–log plot shown in Fig. 3b, reveals that the behavior of \(\langle x^2 \rangle\) in this time regime can be described in terms of a power law, \(t^\alpha\), which is the standard method of parameterization of anomalous diffusion. The slope \(\alpha\) ranges from \(\alpha = 1.0\) for the \(\sigma_i = 0\) cm\(^{-1}\) case to \(\alpha = 0.6\) when \(\sigma_i = 4\sigma_{\text{SS}}\). The orientationally disordered case leads to an intermediate value of \(\alpha = 0.8\). Instead of using Eq. (13), the motion of the exciton over this time range can be described using the standard expression for anomalous diffusion [35].
\[
\langle x^2 \rangle = At^\alpha
\] (14)
Both the prefactor \(A\) and the exponent \(\alpha\) depend on the relative amount of inhomogeneous broadening. This can be
seen in Fig. 4a, which plots \( \ln(\langle x^2 \rangle) \) versus \( \ln(t/\tau_{\text{hop}}) \) for different values of \( \frac{\sigma_{\text{inhom}}}{\sigma_{\text{hom}}} \). Within this range, \( \alpha \) ranges from 1.0 (purely diffusive motion) to 0.5. The dependence on \( \frac{\sigma_{\text{inhom}}}{\sigma_{\text{hom}}} \) can be described roughly as an offset Gaussian, and saturates at a value \( \alpha = 0.5 \). The prefactor \( A \) has a much stronger dependence on the relative amount of disorder, as shown in Fig. 4b. It is the rapid decay of \( A \), proportional to the nearest neighbor hopping probability, that is most responsible for the slowdown seen in our simulations.

An important question is whether the exciton motion is truly subdiffusive at all times, or whether it eventually converges to normal diffusion if provided enough time to explore the disordered energy landscape. For truly subdiffusive motion, \( \alpha < 1.0 \) and the derivative \( \frac{d\langle x^2 \rangle}{dt} \) will always be time-dependent. On the other hand, it is possible that the exciton motion only requires a finite amount of time to average over the different environments before it settles down to purely diffusive motion, albeit with a much slower rate. This latter type of behavior is indeed what we observe in our model system with Gaussian energetic disorder. To illustrate this phenomenon in a universal way, we use the reduced variables \( \frac{x^2}{R^2} \) and \( \frac{t}{\tau_{\text{FRET}}} \) to remove any dependence on the initial hopping time and to be able to compare results using different lattice spacings. Using these variables, we numerically evaluate the quantity \( \frac{d\langle x^2 \rangle}{d(\frac{t}{\tau_{\text{FRET}}})} \) for simulations with orientational disorder only and \( \frac{\sigma_{\text{inhom}}}{\sigma_{\text{hom}}} = 0 \). For normal diffusion in the absence of disorder, this derivative is given by

\[
\frac{d\langle x^2 \rangle}{d(\frac{t}{\tau_{\text{FRET}}})} = \frac{d(2Dt)}{d(\frac{t}{\tau_{\text{FRET}}})} = \frac{2BR^6(1/R^3)^{4/3}}{\tau_{\text{fl}}} \tau_{\text{FRET}} R^2 = 2B
\]

In Eq. (15) we have used the definition of \( \tau_{\text{FRET}} \) from Eq. (2a). Fig. 5 shows the asymptotic behavior of \( \frac{d\langle x^2 \rangle}{d(\frac{t}{\tau_{\text{FRET}}})} \) for several different lattice spacings \( R \) and for two different values of \( \Delta_{\text{ss}} \). In these cases, the derivative becomes constant (i.e. the motion becomes diffusive) only after \( \frac{t}{\tau_{\text{fl}}} \sim 100 \). In our model system, \( R = 1 \text{ nm} \) and \( \tau_{\text{fl}} = 1.0 \text{ ns} \). Given a \( \tau_{\text{FRET}} = 143 \text{ fs} \), the transition to diffu-
sive behavior occurs at around 15 ps. With a larger intersite spacing \( R = 3 \text{ nm} \), \( \tau_{\text{FRET}} \approx 100 \text{ ps} \), and the exciton can never establish truly diffusive motion within its lifetime. Note that the asymptotic value of the derivative in Fig. 5 is less than what is predicted by Eq. (15). One explanation for this discrepancy is that it may be impossible to define an ‘effective \( R_0 \)’ that allows the physical picture underlying Eq. (1) to be maintained at long times. Even in the case of dipole–dipole transfer, the exact value of \( B \) depends on the detailed lattice structure and transfer mechanism [11–13]. Lastly, preliminary results suggest that a similar crossover from subdiffusive to slow diffusive motion occurs for energetic disorder as well, and that this crossover is different for different amounts of disorder. A complete study of this behavior is beyond the scope of the current Letter, but will be the subject of further investigation.

The fact that the exciton requires a nonzero number of transfer events to establish diffusive motion has implications for the use of Eq. (1) to make predictions about how \( D \) and \( L_D \) change as we vary molecular parameters. Eq. (1) predicts that lengthening the lifetime \( \tau_{\text{fl}} \) and decreasing the intersite spacing \( R \) would increase \( D \) and \( L_D \). For example, suppose a value for \( L_D \) is experimentally measured for a dilute sample of chromophores. Eq. (1) predicts that the diffusion constant scales as \( 1/R^2 \) and \( L_D \) scales as \( 1/R^2 \), and thus increasing the chromophore density should dramatically increase the diffusion length. But the expected improvement in \( L_D \) may very well be thwarted by the fact that the diffusion rate measured in the dilute sample with static disorder cannot necessarily be extrapolated to the more concentrated sample. The measured diffusion length in a dilute sample reflects a non-equilibrium motion that is never truly diffusive, while the greater number of hops in a concentrated sample means that the exciton can settle down to an asymptotic diffusion motion that is considerably slower than predicted by Eq. (1). Finally, the presence of a nonzero Stokes shift \( \Delta_{\text{SS}} \) does not affect the qualitative behavior of our results. This is shown in Figs. 4a and 4b, where the dependence of \( x \) and \( A \) on \( A_{\text{SS}} \) are very similar for \( \Delta_{\text{SS}} = 0 \text{ cm}^{-1} \) and \( \Delta_{\text{SS}} = 220 \text{ cm}^{-1} \). The only significant discrepancy is that the initial value of \( A \) is smaller for the \( \Delta_{\text{SS}} = 220 \text{ cm}^{-1} \) case because the initial transfer rate is slower. Similar behavior can be seen in Fig. 5, where the \( \Delta_{\text{SS}} = 220 \text{ cm}^{-1} \) curve overlays the \( \Delta_{\text{SS}} = 0 \text{ cm}^{-1} \) curve.

4. Conclusion

The results reported here suggest that it is dangerous to use Eq. (1) to design strategies for increasing \( D \) in cases where orientational or energetic disorder is present. Preliminary results indicate that our general conclusions are not affected by changing other parameters that affect \( \tau_{\text{FRET}} \), such as \( V_{\text{A}}, \tau_{\text{fl}} \), and \( \epsilon_{\text{peak}} \). The model presented here provides a starting point for analyzing energy transfer in actual molecular systems, where experimental results on energy transfer lengths could be compared to theoretical calculations. In many systems, it is possible that the nanoscale sample morphology, responsible for inhomogeneous broadening and orientational disorder, plays the most important role in determining the exciton diffusion length. Decreasing disorder by orienting the molecules or by reducing local dielectric fluctuations in the sample may provide a way to enhance exciton diffusion and improve performance in fluorescence-based sensors and photovoltaic cells.

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References