Exciton transport in amorphous polymers and the role of morphology and thermalisation

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Abstract
Understanding the transport mechanism of electronic excitations in conjugated polymers is key to advancing organic optoelectronic applications, such as solar cells, organic light-emitting diodes and flexible electronics. While crystalline polymers can be studied using solid-state techniques based on lattice periodicity, the characterisation of amorphous polymers is hindered by an intermediate regime of disorder and the associated lack of symmetries. To overcome these hurdles we have developed a reduced state quantum master equation approach based on the Merrifield exciton formalism. This new approach allows us to study the dynamics of excitons’ centre of mass and charge separation (CS), going beyond the standard model of charge-neutral Frenkel excitons. Using this model we study exciton transport in conjugated polymers and its dependence on morphology and temperature. Exciton dynamics consists of a thermalisation process, whose features depend on the relative strength of thermal energy, electronic couplings and disorder, resulting in remarkably different transport regimes. By applying this method to representative systems based on poly(p-phenylene vinylene) (PPV) we obtain insight into the role of temperature and disorder on localisation, CS, non-equilibrium dynamics, and experimental accessibility of thermal equilibrium states of excitons in amorphous polymers.

1. Introduction

Organic semiconductors (OSCs) are at the forefront of the current research efforts for the development and improvement of optoelectronic technology, such as solar cells [1–3], organic light-emitting diodes [4, 5], thin-film transistors [6–9], sensors and flexible electronics [10–13]. In particular, conjugated polymers are a key class of OSCs for photovoltaic applications, due to their ability to transport electronic excitations, i.e. excitons, over tens of nanometers, together with their low productions cost, ease of fabrication and flexibility [14, 15]. Depending on their chemical composition and fabrication conditions, polymeric semiconductors can be found in a variety of different morphologies characterised by specific exciton transport properties [16].

While the fundamental features of energy and charge transport across crystalline, semicrystalline and amorphous polymers are qualitatively known, the dependence of exciton dynamics on temperature and morphology is still an important area of investigation [17–20]. For example, the introduction of amorphous polymers characterised by high electron mobility has challenged the idea that crystalline ones would be optimal for charge transport [21–26]. The study of exciton transport in amorphous polymers is however hindered by the complexity that arises from their disordered nature, which prevents the use of solid-state techniques based on lattice periodicity. In this intermediate transport regime between band conduction and incoherent hopping, semiclassical techniques such as Marcus theory often fail to reproduce the coherent quantum attributes of the exciton dynamics [27–30], while first-principles calculations like
multiconfiguration time-dependent Hartree (MCTDH) method become computationally intractable due to the large size of the systems of interest [19, 20, 31–34].

An effective alternative to study exciton transport in disordered OSCs is given by reduced state quantum master equations [15]. These allow for the efficient description of the interaction between excitons and nuclear vibrations, i.e. phonons, and account for both coherent and incoherent dynamics. Quantum master equations have therefore been applied to a variety of exciton transport problems in OSCs, such as natural photosynthetic complexes [35–38], molecular aggregates [39–42], and disordered systems [34, 43]. A key insight from this body of literature is that exciton–phonon interactions have an essential role for exciton transport in OSCs. On one hand, decoherence induced by local and uncorrelated phonon modes is known to improve transport efficiency in disordered systems [36, 44, 45], counteracting weak and strong localisation phenomena, such as Anderson localisation [46–49], that otherwise prevail when dynamics is primarily coherent. On the other hand, strong spatial correlations between bath modes can facilitate the emergence of decoherence-free subspaces, improving transport of certain states in ordered systems [50].

Recently, quantum master equations have also been used to study exciton transport in conjugated polymers, albeit only for the case of crystalline morphologies. In reference [19], Lyskov et al. bridge first-principles calculations to a Lindblad master equation [51–55], and obtain a phenomenological model for triplet exciton dynamics in crystalline poly(p-phenylene vinylene) (PPV). Their results show that, conversely to the case of disordered OSCs, decoherence slows down exciton dynamics in crystalline PPV, inducing a rapid transition from ballistic (coherent) to diffusive (incoherent) transport. However, the model used in reference [19] cannot be directly applied to amorphous polymers, whose difficult theoretical characterisation presents several questions [33, 56–67]. How do temperature and morphology affect exciton transport? What are the features of the dynamical transition between localised and delocalised states? Are thermal equilibrium states experimentally accessible? How does disorder affect charge-separation dynamics?

Here we answer these questions generalising the master equation approach used in reference [19] to conjugated polymers with arbitrary morphology. Firstly, since excited electronic states of amorphous polymers are known to display charge separation (CS) over a few monomers [24, 26], we formulate a master equation for the dynamics of Merrifield excitons [31, 68], i.e. a strongly coupled electron–hole pair. Accordingly, our approach can be seen as a direct extension of the master equations used in references [19, 36–38] for the dynamics of charge-neutral Frenkel excitons [69], characteristic of OSCs with low dielectric constant.

Furthermore, our model, introduced in section 2, provides a rigorous thermodynamic description of exciton–phonon interactions, overcoming the limitations of the phenomenological approach used in reference [19]. There, the authors fit the master equation parameters to MCTDH calculations carried out on small two-monomer subsystems over short time scales. Such approach, affected by artificially short recurrence times, may fail to correctly reproduce the dynamics for long time scales and returns decoherence rates that do not necessarily obey thermodynamics in the long-time limit. Here, instead, we use the Bloch–Redfield formalism to calculate temperature-dependent decoherence rates from the phonons’ correlation functions [53, 70], to then express the dynamics of the exciton’s reduced state using a master equation of the Lindblad form [35, 40–42, 54]. This approach has the additional advantage of providing ensemble average transport properties without calculating many individual stochastic realisations of system–environment dynamics.

In section 3, we use the model to study the exciton transport properties of some representative oligo and poly(p-phenylene vinylene) (OPV and PPV) systems, across different morphologies, from crystalline to highly disordered. These materials are often characterised by inhomogeneity at the microscopic scale. It is therefore useful to consider domains within the material within which the movement of energy (or charge) is coherent, or at least partially coherent. The large scale dynamics can then be treated via continuum or effective hopping models based on the thermalised or average state of the sub-domains [27, 29, 71–74]. The cross-over scale between microscopic and macroscopic descriptions depends on the material in question, and can be set by a hierarchy of coupling strengths within the material, finite disorder correlation lengths or finite experimental time-scales. To study the features of coherent and non-equilibrium exciton dynamics that precedes thermal relaxation, we focus on the transport properties of strongly coupled domains, like individual macro-molecules and closely packed tangles of polymer chains (as depicted in figure 1). This allows us to understand how the microscopic dynamics influences transport over the macroscopic scale, a fundamental and continuing research effort [15, 31, 33, 34, 36, 39, 45, 70, 75–79]. Coherent couplings between domains and their surroundings are then assumed to be weaker than those between domains and their vibrational environment, in accordance with the premises, of generalised FRET, generalised Marcus theory and other approaches found in the literature to study long-scale exciton and charge carriers migration in disordered materials, and treated as a perturbation of the domain’s site energies [15, 30, 32, 80–82].
Disordered media are characterised by inhomogeneity at the microscopic scale. Although coherent fast dynamics at the microscale ultimately influence the macroscopic transport properties, it is useful to treat the scales separately. Localised domains can be defined in terms of disorder correlation lengths, or via energy- or time-scale separations within the material. We consider the features of coherent and non-equilibrium exciton dynamics that precede the thermal relaxation and describe the behaviour within a sub-domain. Once a local domain has reached thermal equilibrium, the macroscopic behaviour can be treated with hopping or continuum models which depend on the parameters of the thermalised state.

Instead of relying on material-specific modelling of polymers, we express our calculations in terms of electronic couplings and thermal energy. This allows us to explore the impact that disorder and temperature have on localisation, charge-separation dynamics and equilibration time scales. Exciton transport is therefore interpreted as a thermalisation process [53, 54, 70, 83–85], whose features vary with the relative strength between thermal energy, electronic couplings and disorder. We show how such differences in electronic coupling determine whether the phonon bath cools or heats the system, with dramatic effects on exciton transport properties. We conclude discussing our results in section 4, where we compare and contrast our findings with those of other works, and outlining the use of our method to exciton transport problems of great importance for optoelectronic applications.

2. Methodology

The exciton transport model that we introduce in this article is based on the following two premises. First, the characteristic times and energies associated with exciton transport in OSCs at room temperature and natural illumination imply that excitons do not interact with each other, as they are sufficiently spatially and temporally separated [15]. Under these circumstances, it is a standard approach to focus on the transport of a single electronic excitation, formally defined by the single-exciton manifold [15, 19, 20, 31, 36–38].

Second, we consider polymeric materials whose structural changes are far slower than the characteristic femtosecond to nanosecond time scales of exciton dynamics, such as for the paradigmatic case of PPV and its amorphous derivative MEH-PPV [24, 26]. Additionally, we assume that the interaction between excitons and rapidly oscillating conformational coordinates like bond-length alternations, here modelled as a bath of independent harmonic oscillators [86], are well described in the weak coupling approximation [15].

Under these assumptions, the transport of a single electronic excitation in OSCs is typically modelled as a quantum stochastic walk of a charge-neutral Frenkel exciton over a network of $N$ nodes [87, 88], each of which represents a monomer or a chromophore of the considered domain [15, 19, 35, 37]. However, motivated by recent results on the electronic excitations of amorphous polymers [24, 26], we here generalise this standard approach and extend the dynamics to charge-separated exciton states using the Merrifield model [31]. In this formalism the states of the single-exciton manifold are here given by the product of the localised single-electron and single-hole bases,

$$B := \{ |jk\rangle \}_{j,h=1}^N,$$

where $|jk\rangle := |j\rangle_e \otimes |k\rangle_h$, and where $|j\rangle_e(|k\rangle_h)$ represents the state of the electron (hole) localised on monomer $j(k)$ of a polymeric material. Every monomer $k$ is also associated with its centre’s position $\vec{r}_k := (x_k, y_k, z_k)$ and a set of local conformational coordinates $Q_k$, such as torsional angles and bond-length alternations, as schematically represented in figure 2. These, together with the bonds between pairs of monomers, define the morphology of the medium and determine the structure of the exciton’s Hamiltonian, as described in the next section.
The exciton Hamiltonian $H_{\text{ex}} = H_0 + H_F + H_{\text{CT}}$ is given by the Coulomb term $H_0$, which defines the energetic landscape associated with electron–hole configurations on the polymeric material, and the Frenkel $H_F$ and charge $H_{\text{CT}}$ transfer terms, which model the coherent transport of energy and charges, respectively. In the electron–hole basis of equation (1), the Coulomb term $H_0$ reads

$$\langle eh|H_0|e'h'\rangle = \delta_{eh}\delta_{eh'} \left( E_0 - \frac{1}{4\pi\epsilon_0\epsilon_r d_{eh}} \right),$$

(2)

where $E_0 = (4\pi\epsilon_0\epsilon_r\epsilon_r)^{-1}$ is the exciton binding energy of electron–hole pairs that are localised within the same monomers, i.e. Frenkel excitons (see table 1). The electron–hole distance, $d_{eh} = r_0 + ||\vec{r}_e - \vec{r}_h||$, is obtained from the distance between two monomers offset by the intrinsic electron–hole distance $r_0$ for Frenkel excitons in the considered polymer [31]. The Coulomb term is diagonal in the electron–hole basis, and vanishes for Frenkel excitons. The morphology of the medium introduces static disorder in this term via the inter-monomer distance $d_{eh}$.

The Frenkel term $H_F$ models the coherent transport of Frenkel excitons and is given by

$$\langle eh|H_F|e'h'\rangle = \delta_{eh}\delta_{eh'} V_F(\vec{r}_e, Q_e; \vec{r}_f, Q_f),$$

(3)

where $V_F(\vec{r}_e, Q_e; \vec{r}_f, Q_f)$ is the strength of the Frenkel coupling between a pair of monomers $j,k$, as a function of the morphology of the medium. Frenkel transfer terms in the Hamiltonian mediate the transport of Frenkel exciton states, which form an $N$ dimensional subset of the full $N^2$ dimensional Hilbert space associated with the single-exciton manifold of the Merrifield model.

Similarly, the charge transfer (CT) term $H_{\text{CT}}$ models the coherent transport of individual charges and is given by

$$\langle eh|H_{\text{CT}}|e'h'\rangle = \delta_{eh}\delta_{eh'} V_{\text{CT}}(\vec{r}_e, Q_e; \vec{r}_f, Q_f) + \delta_{hh'} V_{\text{CT}}(\vec{r}_e, Q_e; \vec{r}_f, Q_f),$$

(4)

where $V_{\text{CT}}(\vec{r}_e, Q_e; \vec{r}_f, Q_f)$ represents the strength of the CT coupling between a pair $j,k$ of monomers, as a function of the morphology of the medium. The CT term can map Frenkel states into charge-separated states and vice versa, and its addition to the Hamiltonian allows exciton states to explore the entirety of the single-exciton manifold.

The dependence of the coupling strengths $V_F$ and $V_{\text{CT}}$ on the morphology of the medium is described in terms of the relative arrangement of pairs of monomers that are conjugated, or close enough to each other.
to allow for weaker through-space couplings. Without loss of generality, $V_F$ and $V_{CT}$ are assumed to be symmetric in the pairs’ indices and to vanish for monomers that are not connected by a bond, or out of range for through-space interactions. An example of the dependence of $V_F$ and $V_{CT}$ on the morphology for PPV-like conjugated polymers is given by equations (15) and (16) in section 3.

### 2.2. Exciton–phonon interaction

Exciton–phonon interactions induce decoherence and relax the exciton states until a steady state is reached. The composite dynamics of exciton and phonons is governed by the system–environment Hamiltonian $H = H_{ex} + H_{ex-ph} + H_{ph}$. The vibrational modes involved in this process, such as bond-length alternations and ring-breathing modes [19, 24, 26], are modelled as a bath of local and independent harmonic oscillators [19, 86]. Let us write the exciton–phonon interaction Hamiltonian $H_{ex-ph}$ as

$$H_{ex-ph} = \sum_i A_i \otimes B_i,$$

(5)

such that each coupling operator $A_i$ acting on the exciton space is associated with a bath operator

$$B_i = \sum_m g_{im} \left( b_i^\dagger b_m^\dagger + b_m b_i \right),$$

(6)

given by a sum over the displacement operators associated with the modes with frequencies $\omega_{im}$, written in terms of creation and annihilation operators. The tensor $g_{im}$ represents the coupling strengths between the modes $\omega_{im}$ and the exciton coupling operators $A_i$. These are assumed to be weak, with respect to the characteristic energies of $H_{ex}$ and $H_{ph}$. In this notation the phonon Hamiltonian reads

$$H_{ph} = \sum_{l,m} \hbar \omega_{lm} \left( b_{l,m} b_{l,m}^\dagger + \frac{1}{2} \right).$$

(7)

The exciton coupling operators $A_i$ model the exchange of energy between the exciton and the vibrational modes. These originate from the interaction between charge carriers and their phonon environment, and can either involve a single monomer, or a bond between two monomers. For example, the interaction between the electron (hole) and vibrational modes concerning monomer $k$ is associated with $|k\rangle\langle k| \otimes 1_h$ (or $1_e \otimes |k\rangle\langle k|$) coupling operators. Conversely, the interaction between the electron (hole) and vibrational modes concerning the bond between a pair $j,k$ of monomers is associated with $|j\rangle\langle k| \otimes 1_h \otimes \text{h.c.}$ ($1_e \otimes |j\rangle\langle k|$) coupling operators.

### 2.3. Master equation

The dynamics of the reduced exciton state $\rho_t$ is governed by a Lindblad master equation [89] that is obtained from the system–environment Hamiltonian $H$ by tracing over the phonon environment [53]

$$\dot{\rho}_t = -\frac{i}{\hbar} [H_{ex}, \rho_t] + \sum_{\omega, j} \gamma_{j\omega}(\omega) \left( A_j(\omega) \rho_t A_j^\dagger(\omega) + \frac{1}{2} \left( A_j^\dagger(\omega) A_j(\omega), \rho_t \right) \right).$$

(8)

The Lindblad collapse operators $A_j(\omega)$ are here given by the spectral representation of the coupling operators $A_i$,

$$A_j(\omega) = \sum_{E_i, E_k} |E_i\rangle\langle E_i| A_j |E_k\rangle\langle E_k|,$$

(9)

where $|E_i\rangle$ are the eigenstates of the exciton Hamiltonian, $H_{ex}|E_i\rangle = E_i |E_i\rangle$, such that $\omega$ matches the Bohr frequencies $E_f - E_i$. The relaxation rates $\gamma_{j\omega}(\omega)$ are obtained from the Fourier transform of the bath correlation functions $\langle B_j(t) B_j^\dagger(f) \rangle = \text{Tr} \left[ B_j(t) B_j^\dagger(\tau) \rho_{ph} \right]$ [53, 54]. Here, $\rho_{ph} = \exp(-\beta H_{ph}) Z^{-1}$ is the steady state of the phonon bath, in thermal equilibrium at inverse temperature $\beta = (\hbar \gamma)^{-1}$, with partition function $Z = \text{Tr} \left[ \exp(-\beta H_{ph}) \right]$ [54].

This general approach, also known as the Bloch–Redfield formalism, allows to obtain relaxation rates from the energy and temperature dependent correlation functions of the bath. The rates obtained this way satisfy thermodynamics and detailed balance condition, leading to the correct thermal equilibrium distribution for long time scales [70]. Here, we obtain a prescription for the dynamics of exciton states in the Markovian approximation, under which condition the master equation can be equivalently expressed in either Bloch–Redfield or Lindblad formalism [70].

In the Markovian limit that characterises equation (8), the bath correlation functions only depend on the time interval $\tau$ between two time steps $t - t' = \tau$ [53, 54]. In general, equation (8) can account for
arbitrary pairwise correlations between bath modes [70, 90]. However, when studying exciton transport in section 3 we approximate the phonon environment to a bath of uncorrelated vibrational modes. While vibrational modes such as bond-length alternations would, in fact, have some degree of spatial and temporal correlations with each other, these may decay rapidly over the length and time scale considered for exciton transport at room temperature [91]. Indeed, it has been shown that a local-bath description is satisfactory even for carbon–carbon bond stretching in highly ordered polymer materials at room temperature [86]. In virtue of the mutual independence of the vibrational modes for each pair of coupling operators $A_l, A_r$, the bath correlation functions reduce to

$$
\langle B_l(t)B_r(0) \rangle = \delta_{ll'} \sum_m g_{lm}^2 \left( (1 + \nu_\beta (\omega_{lm})) e^{-\omega_{lm} \tau} + \nu_\beta (\omega_{lm}) e^{\omega_{lm} \tau} \right),
$$

(10)

where $\nu_\beta (\omega) = (\exp(\hbar\beta \omega) - 1)^{-1}$ is the bosonic distribution function at inverse temperature $\beta$ [53, 54].

To calculate the rates $\gamma_l(\omega)$, the sum over the couplings $g_{lm}$ of equation (10) is replaced with an integral in the frequency domain, $\sum_m g_{lm}^2 \rightarrow \int J_l(\omega) d\omega$, where $J_l(\omega)$ is a spectral density that can be used to sample the coupling strengths $g_{lm}$. To do so we use an Ohmic spectral density $J_l(\omega)$

$$
J_l(\omega) = \frac{\Lambda_l}{\hbar \Omega_l} \exp \left( -\frac{\omega}{\Omega_l} \right),
$$

(11)

where $\Lambda_l = \hbar \int_0^\infty d\omega J_l(\omega)/\omega$ is the reorganisation energy associated with coupling operator $A_l$ [35, 53]. In this way the relaxation rates read

$$
\gamma_l(\omega) = 2\pi J_l(\omega) (1 + \nu_\beta (\omega)) + J_l(-\omega) \nu_\beta (-\omega),
$$

(12)

$$
\gamma_l(\omega) = \frac{2\pi \Lambda_l \omega e^{-|\omega|/\Omega_l}}{\hbar \Omega_l \left( 1 - e^{-\beta \omega} \right)}
$$

(13)

Exciton–phonon interactions also introduce further disorder, which is captured by energy fluctuations $\delta E_l$ in the exciton Hamiltonian, $H_{ex} \rightarrow H_{ex} + \sum_l \delta E_l A_l$ [34, 43]. These are sampled from a normal distribution with zero average and standard deviation $\sigma_l(\beta)$, given by

$$
\sigma_l^2(\beta) = \int_0^\infty d\omega \hbar J_l(\omega) \coth \left( \frac{\hbar \beta \omega}{2} \right),
$$

(14)

as done in references [42, 92]. This disorder is static, as motivated by the assumption of slow conformational dynamics, with respect to the typical time-scale of coherent exciton transport [93]. The addition of such energy fluctuations affects site energies and coherent transfer terms, leading to asymmetry in the CS landscape and promoting localisation in the centre of mass (CoM) dynamics [49, 94, 95].

In the next section we use equation (8) to study exciton transport polymeric domains across different morphologies. Before discussing the results, let us make a few remarks on the approximations that characterise equation (8). First of all, it is worth pointing out that, in equation (8) we have neglected the Lamb-Shift Hamiltonian term. This term accounts for the contributions of the coupling operators $A_l$ to the coherent dynamics of the exciton. Lamb-Shift corrections have often been neglected in exciton transport problems, especially for the case of local and uncorrelated phonon baths [35, 37, 38]. However, when applying equation (8) in section 3 we assume the exciton Hamiltonian to include energy shift arising from the weak coupling with the phonon environment, as prescribed by equation (14). There, exact Lamb-Shift corrections are expected to be well below the precision limit of a qualitative study focussed on order-of-magnitude differences in exciton energies and electronic couplings.

Another important observation is that we have assumed the vibrational modes to be uncoupled with each other, which is the reason why equation (8) does not feature combinations of $A_l(\omega)$ and $A_r(\omega)$ Lindblad operators. It is reasonable to imagine that this approximation would not be justified for some combinations of coupling operators, such as for those vibrational modes coupled with the same monomer. When spatial correlations become important, e.g. when phonon modes are delocalised over several monomers, they can be simply accounted for and included into equation (8) via the addition of terms in $A_l$ and $A_r$, and the associated rates arising from the spatial dependence of the correlation functions $\langle B_l(t), B_r(0) \rangle$ [90]. The presence of strong and long-range spatial correlations allows for the formation of decoherence free subspaces and gives rise to super and subradiance phenomena [96], which have been studied for biological light-harvesting complexes [70], but remain rather unexplored for the case of organic polymers.
Finally, the weak coupling approximation for the exciton–phonon interaction, necessary to obtain equation (8), is arguably the main source of deviations from a rigorous description of the exciton transport. While some vibrational modes, such as those associated with torsional angles and foldings of a polymer chain, are very likely to be well described by a weak coupling approximation, others modes, such as bond-length alternations, can couple strongly with the excitons. In such cases it is possible to overcome the limitations imposed by equation (8) by performing a polaron-transformation \[97–100\], which models the dynamics of an exciton followed by nuclear deformations, i.e. a polaron (or dressed-exciton), using master equations similar to equation (8), such as the secular polaron-transformed Redfield equation \[33, 34, 43, 81, 101–105\].

3. Results

We now use equation (8) to study room-temperature exciton transport in some representative conjugated oligomers and polymers, exploring the transition from ordered to disordered morphologies. To highlight the transient features of coherent and non-equilibrium dynamics we consider both initially delocalised and localised states. The former are representative of photoexcitation. The latter is expected to be relevant for the case of energy transfer from a donor to a chromophore in resonance with the acceptor, and have been previously considered in the reference \[19\] for the case of crystalline PPV.

To compare our findings with previous results, we base our calculation upon the electronic properties of OPV and PPV, used in references \[19, 31\]. In particular, we focus on the following systems. First, we consider a short OPV hexamer to explore CoM and CS dynamics with a full Merrifield exciton approach, in section 3.1. Then, in section 3.2, we model a long PPV polymer with 51 repeated unit to explore intrachain Frenkel exciton dynamics across different morphological regimes. Finally, we examine the role of intrachain and interchain transport and its dependence on electronic coupling strength in section 3.3, by looking at Frenkel exciton transport in OPV oligomers.

The different regimes of disorder, from crystalline to amorphous, are here achieved sampling torsional angles and bond length-alternations from a normal distribution with zero average and tunable standard deviation. The functional dependence of Frenkel and CT terms on the relative arrangement between two conjugated monomers, given by \(V_C(d, \theta) = f(d)\Theta_F(\theta)\) and \(V_{CT}(d, \theta) = f(d)\Theta_{CT}(\theta)\), respectively, is calculated upon their distance \(d\) and the relative angle \(\theta\) between the two monomers’ planes. The angular dependence \(\Theta_F(\theta)\) and \(\Theta_{CT}(\theta)\) is modelled as in reference \[31\],

\[
\Theta_F(\theta) = (j_4 - j_0)\cos^4 \theta + (j_2 - j_0)\cos^2 \theta - 2j_0,
\]

\[
\Theta_{CT}(\theta) = t_0 \cos \theta, \tag{16}
\]

while the dependence on the intra-monomer distance is heuristically modelled with a Gaussian factor \(f(d) = \exp[-(d - r_0)^2/4r_0^2]\).

The parameters used in equations (2), (15) and (16) have been chosen to describe the electronic properties of OPV and PPV, and are based on reference \[31\] (see table 1). The relative permittivity of the considered materials is assumed to be \(\epsilon = 1\) for simplicity. The characteristic electronic couplings associated with Frenkel and charge-transfer terms can be as high as 2 eV, and, thus, much larger than the 26 meV associated with the thermal energy of the phonon bath at room temperature of 300 K. When required, through-space Frenkel couplings are included for non-conjugated monomers that are separated by \(\approx r_0\). These are heuristically modelled using the functional form of \(V_C(d, \theta)\), scaling \(j_4\) by a factor of \(10^{-2}\), to achieve characteristic coupling energies of around 10 meV \[19, 106\].

Reorganisation energies \(\Lambda\) and cut-off frequencies \(\Omega\) associated with vibrational modes define relaxation rates \(\gamma(\omega)\) and energy fluctuations \(\sigma(\beta)\), as prescribed by equation (11) \[53, 54\]. For the considered systems we have chosen reorganisation energies of 50 meV, as motivated by references \[81, 107\]. The cut-off frequency has been chosen to be 1500 cm\(^{-1}\), as motivated by references \[19, 32, 107, 108\].

To propagate an initial exciton state \(\rho_0\) exactly solve the system of linear differential equations associated with equation (8) written in Liouville space \[109\]. In this way we obtain a map \(\Lambda\) for the dynamics of the state \(\rho_\text{e} = \Lambda\rho_0\). Exciton transport properties are studied evaluating time-dependent expectation value and standard deviation of CoM and CS operators. These can be expressed in terms of monomer indices \(\langle e\chi\Delta\rho\rangle = \delta_{\omega\sigma}\rho_{\omega\beta}(e + h)/2\), and \(\langle e\chi\Delta\sigma\rangle = \delta_{\omega\sigma}\rho_{\omega\beta}(e - h)\), as done in reference \[31\]. Alternatively, they can be expressed in terms of monomer coordinates \(\vec{r}_k = (x_k, y_k, z_k)\), by replacing \(\epsilon(h)\) with a given Cartesian coordinate, such as \(x_k(x_0)\).

Localisation properties of Frenkel states are inferred from purity, \(P[\rho_\text{e}] = \text{Tr}[\rho_\text{e}^2]\), and average inverse participation ratio (IPR) \[29, 34, 66, 107, 110\]. Let \(\rho = \sum_k \rho_k |\vec{r}_k\rangle \langle \vec{r}_k|\) be expressed in its eigenbasis \(|\vec{r}_k\rangle\)
and let \( \{ |n\rangle \} \) be the sites basis, then

\[
\text{IPR}(\rho) = \sum_k p_k \left( \sum_n |\langle n|\psi\rangle|^4 \right)^{-1},
\]

i.e. the weighted sum of the IPR = 1/\( \sum_n |\langle n|\psi\rangle|^4 \) for each pure state \( |n\rangle \) making up the density operator \( \rho \) [34, 76]. From the IPR, delocalisation length can be estimated using \( l = (\text{IPR}(\rho))^{1/4} \) for a \( d \)-dimensional system [34]. Since the considered systems are either one-dimensional or ensembles of coupled one-dimensional systems we estimate the delocalisation length simply using \( \text{IPR}(\rho) \).

### 3.1. OPV hexamer

This system consists of six conjugated monomers and it is studied with a full Merrifield exciton approach, i.e. including all the possible CS states. For each morphology, we consider initially localised and delocalised Frenkel excitons, as shown in figure 3. For comparison, a similar system was studied in reference [31] with an MCTDH method, requiring around \( 10^6 \) configurations for its numerical implementation, as opposed to the 36 required for the solution of equation (8) [111].

The crystalline morphology, shown in figure 3 (top), is obtained for a perfectly planar arrangement of the monomers with constant bond-length alternation and no static disorder. It is characterised by trivial CS dynamics, which remains constant and equal to zero for all times. An initially localised exciton undergoes an initial ultrafast ballistic transport regime (1–10 fs), followed by a diffusive transport regime that lasts for the first 100 fs. During the evolution the partial states of electron and hole are perfectly symmetric for both initially localised and delocalised states, as shown in the histograms insets of figure 3 representing the population (not in scale) of the partial states of electron (black bars) and hole (light gray bars) on each site at a given time.

The semicrystalline morphology, an instance of which is shown in figure 3 (middle), is obtained for torsional angles normally distributed with standard deviation of 0.5 rad. The presence of disorder allows for...
a non trivial CS dynamics, thus reducing the energy barrier required for CD of the exciton. Despite the CoM dynamics has similar features to those of the crystalline morphology, asymmetry in the partial states of electron and hole is generally present both during the evolution and in the steady states.

The amorphous phase, an instance of which is shown in figure 3 (bottom), is obtained for torsional disorder with standard deviation of 1 rad. It is characterised by noticeable CS dynamics, with electron–hole separation over a few monomers, as previously reported in reference [24], lasting for hundreds of femtoseconds. Such CS dynamics can considerably reduce the CD energy for relatively long time spans of hundreds of femtoseconds. Remarkably, high-disorder allows for the formation of long-lived non-equilibrium states, before thermal equilibrium is reached around 100 ps. Exciton lifetimes may be shorter than the time required to reach thermal equilibrium in such systems. This implies that thermal equilibrium states of the excitons are generally not experimentally accessible.

3.2. PPV polymer

We now consider a PPV polymer with 51 repeated units in its crystalline and amorphous form. For each morphology we consider initially localised and delocalised Frenkel excitons, as shown in figure 4.

For the crystalline morphology, the dynamics of initially localised Frenkel excitons is characterised by a transition from ballistic to diffusive transport during the first 100 fs, as shown in figure 4 (top-left). This is in analogy with the results of reference [19]. The remaining part of the dynamics consists in a relaxation process that guides the exciton towards thermal equilibrium. Similarly, initially delocalised excitons diffuse through the medium by means of such relaxation process (top-right). The absence of disorder in the sites energies and electronic couplings allows for the formation of highly delocalised steady states, with IPR > 30.

However, in contrast with the results of reference [19], steady state populations are not evenly spread across the polymer, and thus only partially mixed. This is because the decoherence model used in reference [19] does not account for the spectral response between exciton coupling operators and the phonon bath. The results of reference [19] can be qualitatively reproduced using equation (8) by replacing the Lindblad operators $A_l(\omega)$ with the coupling operators $A_k$ and the associated relaxation rates $\gamma_l(\omega)$ with frequency independent rates $\gamma_l$. In such simplified limit, steady states become diagonal in the sites basis. Here, instead, we use a Bloch–Redfield approach for rates and dissipators and obtain the correct thermal equilibrium states, which are diagonal in the exciton Hamiltonian basis.

As disorder is increased, localisation becomes more evident, undermining the ultrafast ballistic transport regime that would otherwise characterise the dynamics of initially localised excitons for the crystalline...
Figure 5. Exciton transport for an arrangement of three semicrystalline OPV octamers with weak ($j_4 = 100$ meV) (top) and strong ($j_4 = 1$ eV) (bottom) electronic couplings at room temperature $T = 300$ K. Dynamics of initially localised (delocalised) Frenkel exciton is shown on the left (right). The thermal energy of around 25 meV associated with $T \approx 300$ K is sufficient to spread the exciton over the entire domain in the case of weak couplings. However, it is not enough for such migration to occur for domains characterised by strong couplings, which, in contrast, exhibit high-purity and low CoM standard deviation. Expectation value (solid lines) and standard deviation (shaded areas) of CoM (blue) are expressed in the sites basis. Delocalisation is monitored by purity (dashed light blue lines) and average IPR in the sites basis (round yellow markers). The insets schematically represent the populations (in arbitrary units) of the exciton on each site at a given time.

morphology. The amorphous morphology, an instance of which is shown in figure 4 (bottom-left), is characterised by sub-diffusive exciton transport within the first 100 fs, followed by thermal relaxation. States are remarkably less delocalised both during the dynamics and at equilibrium, with $\text{IPR} \approx 6$ and CoM standard deviations much lower than for the crystalline morphology. The slower thermalisation induced by disorder accentuates the difference between initial states, and extends the lifetime of transient features that anticipate thermal equilibrium. The latter may requires times longer than the typical exciton recombination times, with implications on the observably of thermal equilibrium states for amorphous polymer domains.

To further examine the relation between morphology and exciton delocalisation we study the IPR of steady states at room temperature for different morphological regimes. To do so we vary the standard deviation $\sigma_\theta$ for the random torsional angles between 0 (crystalline) and 1 rad (amorphous), sampling 100 different PPV polymers with 51 monomers for each morphology. The results, presented in figure 6(a) (left), show the high sensitivity of exciton delocalisation to conformational defects. Delocalisation rapidly drops from $\text{IPR} \approx 35$ for crystalline polymers to $\text{IPR} \approx 4$ for amorphous ones.

3.3. Dependence on electronic couplings

We now study the dynamics of Frenkel excitons for fixed morphology while varying the strength of the electronic couplings. This allows us to explore the different regimes of exciton transport and thermal equilibrium that are associated with weak and strong electronic couplings. We illustrate such difference by looking at the dynamics of initially localised and delocalised Frenkel excitons in a system given by three closely arranged OPV octamers that interact via through-space couplings, shown in figure 5. To vary the strength of the electronic couplings we tune the Frenkel coupling constant $j_4$ (see table 1). Through-space couplings have been modelled as discussed in section 3.

Systems with weak electronic couplings are here obtained using $j_4 = 100$ meV, with Frenkel coupling strength distributed between 10 and 100 meV due to disorder. For these systems coherences rapidly vanishes within the first 10–20 fs. As shown in figure 5 (top), exciton transport is incoherent both during an initial intrachain transport over one oligomer and during the slower interchain transport across the different oligomers. The thermal energy is sufficient to populate several eigenstates of the exciton Hamiltonian. Thermal equilibrium is therefore characterised by low-purity and large CoM standard deviation.

Systems with strong electronic couplings are here obtained using $j_4 = 1$ eV, with Frenkel coupling strength distributed between 0.1 and 1 eV due to disorder. These systems display faster intrachain dynamics,
with respect to those characterised by weak couplings, followed by slow and incoherent interchain transport. However, the thermal energy is not high enough to populate several states of the exciton Hamiltonian, therefore the steady states are rather pure and localised around the most energetically favourable clusters of conjugated monomers, as shown in figure 5 (bottom-left). This is to be attributed to the stronger coupling between a few neighbouring monomers that are in resonance with each other.

To systematically explore the dependence of exciton delocalisation on the strength of the electronic couplings (and thus on the thermal energy) we study IPR, purity and CoM standard deviation of transient (100 fs) and steady states of semicrystalline oligomers. To do so, the characteristic strength $j_4$ of Frenkel couplings is varied from 1 meV to 1 eV. For each coupling regime we sample 100 OPV oligomers with 10 repeated units (OPV10) and fixed semicrystalline morphology ($\sigma_\theta = 0.5$ rad). As shown in figure 6(b) (right), the average IPR is only slightly affected ($\approx 10\%$) by a variation of two orders of magnitude of electronic couplings strength. However, transport properties change dramatically, with CoM standard deviation and purity varying remarkably for both transient and steady states.

3.4. Final remarks

Using the model introduced in this article the dynamics of excitons in conjugated polymers is understood as a quantum thermalisation process, whose features strongly depend on the amount of disorder (i.e. morphology) and on the relative magnitude of thermal energy and electronic couplings (i.e. temperature). For initially localised excitons, the non-equilibrium dynamics is characterised by an ultrafast and ballistic transport transient. An intermediate diffusive or sub-diffusive transport process that occurs both through-bond and through-space characterises both initially localised and delocalised excitons. The dynamics culminates with thermal relaxation. Increasing disorder enables localisation, thus decreasing delocalisation lengths and IPR and hindering the efficacy of exciton transport.

Our results show that the amorphous phase is characterised by the formation of long-lived non-equilibrium states whose relaxation time-scale can be longer than the average exciton lifetime. Firstly, this slow thermal relaxation has fundamental implications on the experimental observability of thermal equilibrium states. Secondly, these transient non-equilibrium states are often characterised by significant charge-separation and low delocalisation. As shown in reference [112], this combination is key to lower the energetic barrier for CD to occur and efficiently generate currents in PV devices [113].

Another important observation concerns the role that the strength of electronic couplings has on the efficiency of energy transport. In polymers characterised by weak electronic couplings, of the order 10–100 meV, the environment heats the system, driving the excitons to low-purity thermal states, with non-negligible populations across the whole spectrum of energy eigenstates of the exciton Hamiltonian. Even though the intrinsic localisation lengths are low due to the presence of disorder, the thermal energy of the phonon bath (around 26 meV at room temperature) is sufficient to populate monomers that are far apart from the initial exciton location. In contrast, in materials characterised by strong Frenkel and charge-transfer couplings ($\approx 1$ eV), the phonon environment cools the system, leading the excitons to
high-purity thermal states, with low-energy eigenstates of the exciton Hamiltonian being the only few populated ones.

While low electronic couplings are generally associated with poor energy transport properties in ordered OSCs, our results reveal that low couplings can improve transport properties in a disordered system at room temperature. As shown in figure 6, low electronic couplings lead to significantly larger spread of the exciton probability distribution over a polymer and lower purity of the exciton states. These features indicate enhanced transport properties due to coherent delocalisation or stochastic occupation of low-energy delocalised states [66]. For this reason, despite the slower intrachain transport, systems with weak electronic couplings can display a more efficient transport mechanism over the picosecond time-scale at room temperature. This becomes particularly important for triplet excitons, which typically have lower mobility and longer lifetime than singlet excitons.

4. Conclusions

In this article we have developed a reduced state quantum master equation to study the dynamics of Merrifield excitons in conjugated polymers as a function of temperature and morphology of the medium. Using this method we have explored the general features of energy and charge transport in some representative systems based on PPV’s electronic properties, confirming well known paradigms of quantum transport in disordered systems, and revealing non-equilibrium features such as long-lived states and charge-separation dynamics. With this method we show that the main transport features can be deduced from two accessible quantities: the relative strength of electronic couplings compared to the thermal energy, and the amount of disorder.

Our results provide fundamental insight into the role of non-equilibrium exciton dynamics in amorphous polymers. The formation of long-lived non-equilibrium states with low IPR and significant CS is crucial to improve the efficiency of CD in PV devices [112]. Nevertheless, it is still not clear how to take advantage of these transient states. This is because disorder-induced localisation also hinders exciton transport. Finding the right balance between energy transport and CD efficiency is crucial for improving OSCs for PV applications. As discussed in section 3.4, the combination of low-electronic couplings and disorder might indeed prove to be successful for this endeavour.

The method introduced in this work can be adapted to a variety of problems, and uncover features of energy and charge transport in the quantum regime that have not been previously addressed. Equation (8) can be used to study partially ordered structures like polymeric rings, coils, rods and fibres, and determine how these could lead to enhanced energy transport. The main goal of this effort should be to look for different mechanisms that lead to partial or transient exciton delocalisation. The latter is largely responsible for the record-breaking exciton transport efficiency show in reference [86], where the authors reported exciton transport over 100 nm at room temperature in polymer nanofibers.

Beyond the qualitative understanding of exciton dynamics in amorphous polymers, we expect our method to be applicable for the quantitative study of energy and charge transport properties of specific materials. This can be done using a multi-scale approach based on molecular dynamics and first-principle calculations, as demonstrated in references [19, 41, 42, 74]. We also believe that this approach would be useful to study disorder-dependent effects in OSCs, such as trapped-charge induced photoluminescence peak displacement [114, 115] and individual charge-carrier pathways in amorphous polymers [116]. We also anticipate the use of this model for the study of individual polymer chains in solution. Finally, we suggest that our method could be extended to disordered inorganic semiconductor such as amorphous silicon.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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As discussed in section 2 this advantage in terms of computational cost comes at the expense of several approximations that reduce the accuracy of the master equation.

Dynamical disorder can be implemented in this model if conformational coordinates and morphology are expected to vary over time-scales comparable to that of the excitons.