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Charge Mobility Induced by Brownian Fluctuations in π-Conjugated Polymers in Solution

Jessica Ellen Poole[1,2], Djamshid Ahmud Damry[1,3],
Oliver Robert Tozer[1,4], and William Barford[1,2]
[1] *Department of Chemistry, Physical and Theoretical Chemistry Laboratory,*
University of Oxford, Oxford, OX1 3QZ, United Kingdom
[2] *Balliol College, University of Oxford,*
Oxford, OX1 3BJ, United Kingdom
[3] *Worcester College, University of Oxford,*
Oxford, OX1 2HB, United Kingdom
[4] *University College, University of Oxford,*
Oxford, OX1 4BH, United Kingdom

Abstract

We study the motion of a doped charge in a π-conjugated polymer chain in solution subject to Brownian fluctuations. Specifically, we take poly(para-phenylene) to be our model system where the Brownian fluctuations cause rotational motion of the phenylene rings. The instantaneous torsional fluctuations cause Anderson localization of the charge wavefunction, with the lower-energy spectrum being composed of local ground states and the higher-energy spectrum being composed of quasi-extended states. At low temperatures, additional charge localization occurs via torsional relaxation. The dynamical torsional fluctuations lead to two distinct modes of motion of the charge: adiabatic and non-adiabatic. Adiabatic motion is a ‘crawling’ motion of the charge along the polymer chain while the charge remains in its local ground state. Non-adiabatic motion is a rapid ‘hopping’ motion as the charge is excited into higher energy quasi-extended states and travels ballistically along the chain before relaxing into a local ground state. The adiabatic motion dominates at low temperatures, and exhibits a linear temperature dependence and thus a constant zero-field charge mobility. Non-adiabatic motion begins to dominate as the temperature is increased, as the charge is thermally excited into higher energy states. At high temperatures the diffusion constant becomes almost temperature independent, indicating a decrease in the charge mobility with increasing temperature, which we attribute to the charge localization length being a decreasing function of temperature at high temperatures.

I. INTRODUCTION

Owing to the potential electronic device applications of π-conjugated polymers, the role of conformational disorder and polaronic effects on charge transport in polymers is of topical interest. Early work by Prins *et al.*[1] studied charge transport in polymers with static torsional disorder via the time-dependent Schrödinger equation. They showed that the disorder causes initially ballistic transport to become diffusive. Hultell and Strafström[2] also used the time-dependent Schrödinger equation to model charge mobility in polymer chains with static disorder, but in addition, they introduced polaronic effects via bond relaxation. Subsequently, they also considered polaronic effects via torsional relaxation[3]. In both of these works the authors showed that when driven by an electric field the charge transport exhibited both diffusive and hopping behaviour.

The role of thermally driven torsional fluctuations on charge transport has been studied by Albu and Yaron[4], who investigated charge transport on a polymer chain in solution where the torsional dynamics are driven by Brownian fluctuations. They considered the adiabatic regime (by assuming that the charge remains in its ground state) and found polaronic, diffusive behaviour. Fornari and Troisi[5] used a Fermi Golden Rule (FGR) formalism to investigate the role of both static and dynamic torsional fluctuations on charge transport, while also including polaronic effects via bond relaxation. This approach necessarily models non-adiabatic processes, with the authors predicting both short range and longer range hops via more delocalized states (as described in more detail below).

In this work we make a link between ref[4] and ref[5] by extending the work of ref[4] to include non-adiabatic processes. In particular, we consider a polymer chain in solution whose monomers are subject to Brownian fluctuations. The Brownian motion drives the torsional fluctuations which, now being time-dependent, causes changes to and transitions between the quasi-stationary states.

In addition to the torsional fluctuations causing charge delocalization, the instantaneous torsional disorder also causes charge localization. As is well known in one-dimensional systems, disorder localizes all quantum states. However, as observed by Malyshev and Malyshev[6] in their study of excitonic states in disordered J-aggregates via the Frenkel exciton model (mathematically equivalent to Eq. (1) of this paper), the low-energy spectrum is composed of superlocalized, virtually nodeless states that are non-overlapping and spacefilling[6]. These states are called local ground states (LGSs). Higher energy states, however, are nodeful and more delocalized; these are called quasi-extended states (QESs). These ideas were extended to π-conjugated polymers using the Frenkel exciton model by Makhov and Barford[7]. Similar observations on exciton localization in polymers via atomistic models have been made by Barford and Trembath[8] and Ma *et al.*[9]. Likewise, similar observations on charge localization in polymers via atomistic models have been made by Qin and Troisi[10]. As we show in this paper, QESs play a key role in charge mobility.

Since the torsional degrees of freedom are coupled to the electronic degrees of freedom, an additional localization mechanism is the polaronic self-localization of the charge via torsional relaxation. For charges, however, the self-trapped polaron binding energy via torsional relaxation is rather small (equivalent to ~ 260 K), so such self-localization is only a dominant process for $T \leq 260$ K.

As we show in this paper, there are two mechanisms for charge mobility from an initially self-localized polaron, where – as explained in §III – the term 'polaron' refers to a self-localized Landau polaron at low temperarures and an Anderson localized polaron at high temperatures. First, at low temperatures there is small-displacement diffusive motion of the polaron as a whole along the polymer chain caused by partially planarization of the torsional angles. This is the adiabatic motion observed by Albu and Yaron[4]. Second, at higher temperatures there are thermally activated transitions from polarons to higher energy more delocalized QESs. This is the non-adiabatic motion modelled via the FGR by Fornari and Troisi[5].

In this paper we take poly(para-phenylene) (PPP) as our model system. We model the torsional dynamics via the Langevin equation. The motion of the charge is modelled by projecting the instantaneous eigenstates of a coarse-grained tight-binding model onto the charge wavefunction of the previous time step, and selecting the eigenstate with the largest overlap. The methodology employed here follows that described in ref[11] to model exciton dynamics induced via torsional fluctuations (see also ref[4] and ref[12]). The general methodology is described in the next section. In Section III we discuss the temperature dependence of the polaron localization length. Section IV contains our results, and we conclude in Section V.

II. MODEL AND METHODOLOGY

A. Coarse-Grained Tight-Binding Model

The poly(para-phenylene) chains are modelled using a coarse-grained tight-binding model. In this model, the polymer chain is formed of N sites, with each site representing one of the phenylene rings in the polymer chain. The tight-binding Hamiltonian describing the motion of the doped electron, H_{TB}, is then given by

$$H_{TB} = E_0 \sum_{n=1}^{N} c_n^\dagger c_n - \sum_{n=1}^{N-1} t_n (c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n) \tag{1}$$

where $c_n^\dagger$ (c_n) creates (destroys) an electron in the LUMO on monomer n. t_n is the charge transfer integral across the nth bond, which links monomers n and $(n+1)$. Since the p_z atomic amplitude on the bridging carbon atoms is[13] $1/\sqrt{3}$,

$$t_n = (t_s/3)\cos\theta_n, \tag{2}$$

where θ_n is the torsional angle between monomers n and $(n+1)$ and $t_s = 2.2$ eV. $E_0 = t_p$ is the LUMO energy of the electron, where $t_p = 2.4$ eV. An equivalent Hamiltonian describes the hole motion via the HOMOs, except that in this case t_n has the opposite sign.

The state vector of the doped electron, $|\Psi\rangle$, is then formed by a linear combination of single monomer LUMO basis states, $|n\rangle$, as

$$|\Psi\rangle = \sum_{n=1}^{N} \Psi_n |n\rangle \tag{3}$$

where Ψ_n is the electron wavefunction.

In solution, the dihedral angle across the nth bond is assumed to have an equilibrium value, θ_n^0, of $\pm 40^\circ$ due to the steric interactions betwen adjacent monomers. In the absence of a charge the torsional mode is assumed to behave harmonically, such that there is a restoring torque on phenylene ring n

$$\Gamma_n^{el} = -K(\delta\theta_{n-1} - \delta\theta_n), \tag{4}$$

where $\delta\theta_n = (\theta_n - \theta_n^0)$ is the deviation of the torsional angle, θ_n, from the equilibrium torsional angle, θ_n^0. The spring constant for the torsional modes of PPP, K, has a value of

1.13 eV. If a torsional mode is behaving harmonically, then in thermal equilibrium there is a Gaussian distribution of bond angles with a standard deviation given by[8]

$$\langle \sigma_\theta \rangle = \left(\frac{k_B T}{K} \right)^{\frac{1}{2}} \tag{5}$$

where k_B is the Boltzmann constant and T is the temperature.

In addition to the harmonic torque, there is a net torque on the phenylene rings due to the presence of the doped charge, resulting in the formation of a self-localized charge Landau polaron at low temperatures. From the Hellmann-Feynman theorem, this torque is

$$\begin{aligned} \Gamma_n^{ch} &= -\left\langle \Psi \left| \frac{\partial H_{TB}}{\partial \phi_n} \right| \Psi \right\rangle \\ &= -(t_s/3)\Psi_n \left(\Psi_{n+1} \sin\theta_n - \Psi_{n-1} \sin\theta_{n-1} \right), \end{aligned} \tag{6}$$

where ϕ_n is the torsional coordinate of the nth ring, such that $\theta_n = (\phi_{n+1} - \phi_n)$. The total systematic torque is

$$\Gamma_n^{syst} = \Gamma_n^{el} + \Gamma_n^{ch}. \tag{7}$$

B. Brownian Dynamics

The Brownian dynamics of the phenylene rings are modelled by the Langevin equation. The equation of motion for phenylene ring n is given by

$$I \frac{d\Omega_n(t)}{dt} = -I\gamma\Omega_n(t) + \Gamma_n^{syst}(t) + R_n(t), \tag{8}$$

where $I = 9.119 \times 10^{-27}$ eV s^2 is the moment of inertia of a phenylene ring about its rotational axis, $\Omega_n = d\phi_n/dt$ is its angular velocity, and $R_n(t)$ is the stochastic torque on the ring due to the random fluctuations in the solvent. γ is the friction coefficient for the specific solvent and condition; we set $\gamma = 10^{12}$ s^{-1}.

By the fluctuation-dissipation theorem[14], the distribution of random torques, $R_n(t)$, is given by

$$\langle R_n(0) R_m(t) \rangle = 2I\gamma k_B T \delta_{mn} \delta(t). \tag{9}$$

In addition to being both spatially and temporally uncorrelated, these torques are also assumed to be independent of the angular velocity of the phenylene ring and independent of the systematic torque, Γ_n^{syst}. These stochastic torques then form a Gaussian distribution with a standard deviation of

$$\sigma_R = (2I\gamma k_B T)^{\frac{1}{2}}. \tag{10}$$

We implement the Brownian dynamics using the algorithm described by van Gunsteren and Berendsen[15].

C. Charge Dynamics

The torsional dynamics renders the tight-binding Hamiltonian time-dependent. However, since the torsional degrees of freedom are much slower than the electronic degrees of freedom, we assume that the charge state vector, $|\Phi(t)\rangle$, evolves quasi-adiabatically. That is, its evolution is determined by calculating the instantaneous eigenstates of the Hamiltonian at time $(t + \delta t)$, i.e., $\{|\Psi(t + \delta t)\rangle\}$, and projecting them onto the target charge state vector at the previous time step t, i.e., $|\Phi(t)\rangle$. The eigenstate with the largest overlap is selected to be the target charge state vector at the next iteration, i.e., $|\Phi(t + \delta t)\rangle$.

It should be noted that the projection of the instantaneous wavefunction onto an instantaneous eigenstate corresponds to a ‘measurement’ of the system, and thus in principle the time-step, Δt, becomes a parameter in the simulation. It would be preferable to solve the time-dependent Schrödinger equation (see, e.g., ref[1–3]). However, the Ehrenfest approximation fails when coupled to a heat bath, because the quantum and classical degrees are uncorrelated, thus inhibiting relaxation processes[16]. Appendix A discusses the role of the step size, Δt. We take $\Delta t = 10^{-14}$ s, which for the temperature ranges considered is small enough to accurately model torsional dynamics, but large enough to avoid ‘measurement’ problems.

Typically, we performed the simulations on polymers with 200 monomers (i.e., 200 coarse-grained sites). During the simulation the boundaries of the chain were displaced, as described in ref[11], to ensure that on average the charge remained in the centre of the chain. Each simulation of the mean-square-distance travelled at a particular value of temperature was performed over 200 realizations of the Brownian fluctuations.

III. POLARONS

A polaron is a localized charge wavefunction. In the field of π-conjugated polymers, polarons are often regarded as self-localized wavefunctions arising from the coupling of a charge to a set of harmonic oscillators (e.g., bond vibrations or torsional fluctuations). This coupling 'self-traps' the charge and if the oscillators are sufficiently slow, the self-trapping causes self-localization and 'Landau' polarons. As discussed in ref[17], the high-frequency C-C bond oscillations are not expected to self-localize charges, whereas the low-frequency torsional fluctuations are more likely to do so. Thus, in this work we only consider polaron self-localization via the torsional fluctuations. The calculated binding energy of the polaron is 0.0225 eV, corresponding to a temperature of 261 K.

Another mechanism to localize charge wavefunctions (and hence form polarons) is Anderson localization[18] arising from conformational disorder. The disorder in the dihedral angles causes Anderson localization of the charge wavefunctions, resulting in the low-energy states being superlocalized into non-overlapping local ground states (LGSs),[6,7]. As these states are essentially nodeless, they can be identified by calculating a signed-value-parameter, SVP, for each state, where[6]

$$\mathrm{SVP} = \left| \sum_{n=1}^{N} \Psi_n |\Psi_n| \right|. \tag{11}$$

A truly nodeless state will have a value of SVP = 1, while a LGS is generally defined as any state where SVP ≥ 0.95. States with a SVP ≤ 0.95 are generally quasi-extended.

Figure 1 shows the the ensemble averaged charge localization length, ℓ, defined as

$$\ell = 5.6\sqrt{\langle R^2 \rangle - \langle R \rangle^2} \tag{12}$$

where

$$\langle R^l \rangle = \sum_{n=1}^{N} R_n^l |\Psi_n|^2 \tag{13}$$

and the factor of 5.6 arises from the ratio between the root-mean-square spread of a LGS and the length of chain it occupies.[8] For $T < 10$ K, ℓ is virtually independent of temperature, because the charge is bound in its self-trapped, self-localized Landau polaron. For T greater than the polaron self-trapped binding energy (~ 260 K), however, ℓ is a decreasing function of temperature, reflecting the behaviour of an Anderson localized polaron whose localization length satisfies[19] $\ell \sim (\sigma_t/t)^{-2/3}$, where σ_t is the standard deviation of the charge transfer integral, t. However, since $t \sim t_s \cos\theta$, $\sigma_t \sim t \tan\theta_0 \sigma_\theta$, where σ_θ is the standard deviation of θ. Thus, since from Eq. (5) $\sigma_\theta \sim T^{1/2}$, we deduce that $\ell \sim T^{-1/3}$. The intermediate temperature range illustrates the cross-over between the low-temperature Landau polaron behaviour to the high-temperature Anderson polaron behaviour. As we show in the next section, the temperature dependence of the polaron size affects the charge mobility.

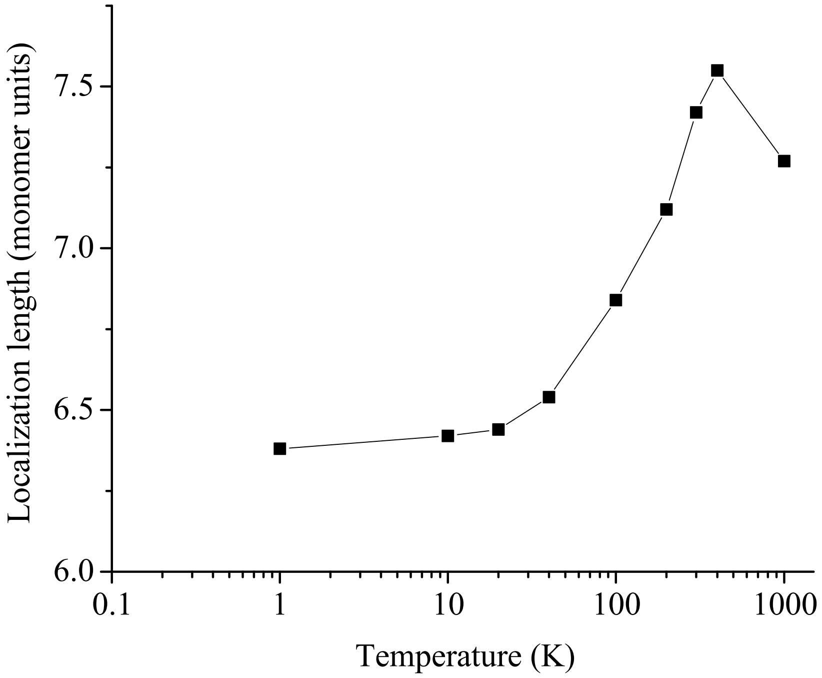

FIG. 1: The mean polaron localization length, ℓ, (in units of the monomer size) as a function of temperature. This is an interpolation between the low-temperature Landau polaron size (which is independent of temperature) and the high-temperature Anderson polaron size (which varies as $T^{-1/3}$). The maximum value of ℓ occurs at $\sim$ 260 K, corresponding to the polaron self-trapped binding energy.

IV. CHARGE MOTION

Assuming that the charge moves diffusively, the mean square distance moved by a charge in a polymer chain in a time t, $\langle L^2 \rangle$, can be expressed as

$$\langle L^2 \rangle = 2D(T)t, \tag{14}$$

where $D(T)$ is the temperature dependent diffusion constant. Figure 2 indicates that the charge motion is indeed diffusive for all temperatures investigated. From the gradients we extract the total diffusion constant, as shown in Fig. 3.

We also extract the adiabatic and non-adiabatic contributions to the diffusion constant, as follows. Adiabatic motion is defined by the signed-value-parameter (Eq. (11)) remaining ≥ 0.95, i.e., the charge remains in a LGS (but not necessarily the global ground state). Since

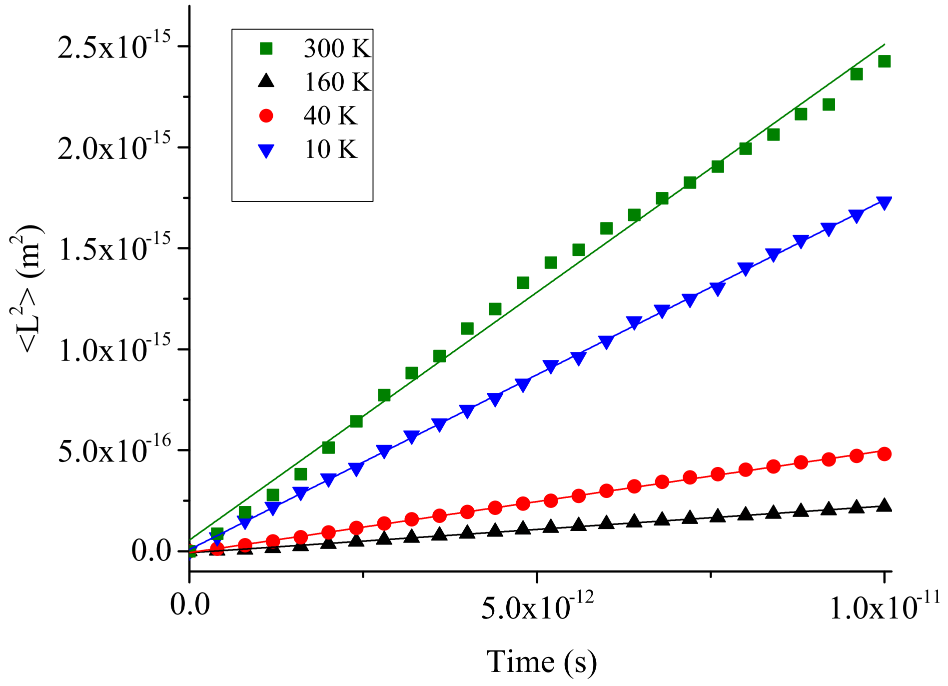

FIG. 2: The mean square distance travelled, $\langle L^2 \rangle$, by a charge along the polymer chain at different temperatures. The motion is diffusive, as shown by $\langle L^2 \rangle$ increasing linearly with time.

transitions between neigbouring LGSs is vanishingly unlikely, because of the very small bond-order-overlap between them, adiabatic motion means slow evolution of the quasi-stationary states. Thus, adiabatic motion corresponds to the polaron moving along the chain as random collisions with the solvent molecules cause rings in one direction to planarize more, and rings in the opposite direction to planarize less, thereby making the polaron 'crawl' around the chain. As the adiabatic movement is likely to be activationless, it is expected to exhibit behaviour predicted by the Einstein-Smoluchowski equation

$$D(T) = \left(\frac{\mu}{e}\right) k_B T, \tag{15}$$

where μ is the zero-field charge mobility. The low-temperature dynamics is entirely adiabatic and, as Fig. 4 indicates, Eq. (15) is satisfied.

In the low-temperature limit (i.e., $T \lesssim 100$ K) the calculated value of $\mu \simeq 100$ cm^2/Vs, with an error of ~ 10 cm^2/Vs, for a value of $\gamma = 10^{12}$ s^{-1}. This applies only when the charge exhibits adiabatic behaviour. Extrapolating the data obtained by Albu and Yaron

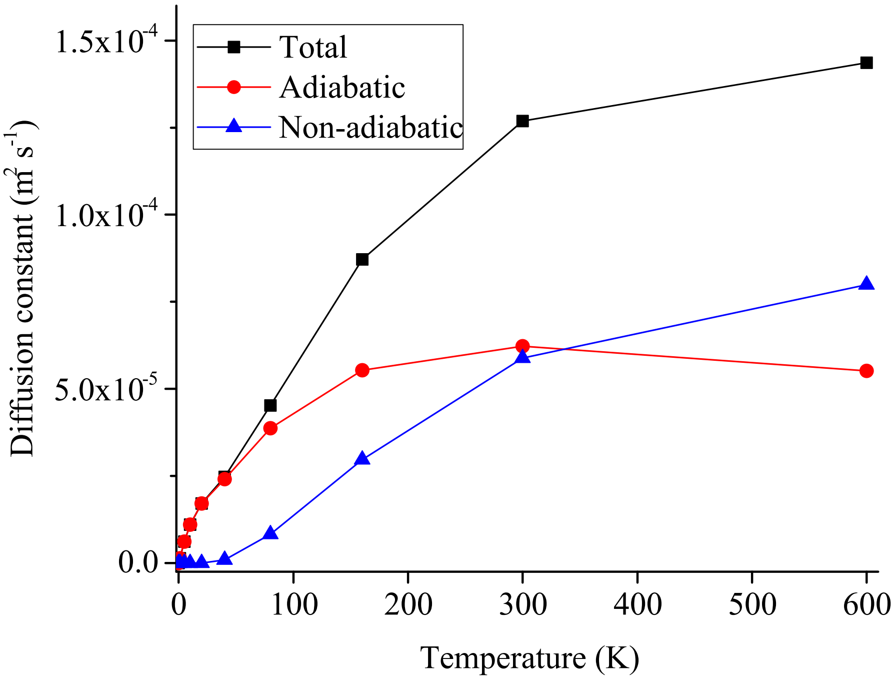

FIG. 3: The charge diffusion constant (squares) along the polymer chain, obtained from Fig. 2, as a function of temperature. Also shown are the contributions from adiabatic (circles) and non-adiabatic (triangles) motion, as defined in the text. Adiabatic motion dominates at low temperatures (see Fig. 4), whereas non-adiabatic motion dominates at higher temperatures.

for their poly(para-phenylene vinylene) calculations[4] to our value of γ, we find that our calculated mobility for PPP is over an order of magnitude larger than theirs. We note that this is the zero-field curvilinear mobility along the chain, and does not correspond to a three-dimensional mobility.

Non-adiabatic dynamics occur when the charge is thermally excited from a localized polaron into a more delocalized electronic state, i.e., a QES. In this case, there is a sharp drop in SVP to typically close to zero. As Fig. 3 indicates, at higher temperatures non-adiabatic motion begins to dominate, and indeed the extent of adiabatic motion decreases. The latter result could be a consequence of the charge being continuously excited into higher states, spending less time in the polaron, and therefore the contribution of the crawling polaron movement to the overall motion is reduced. Alternatively, it could be due to the rings being increasingly less able to planarize (Brownian motion effects increase with increasing

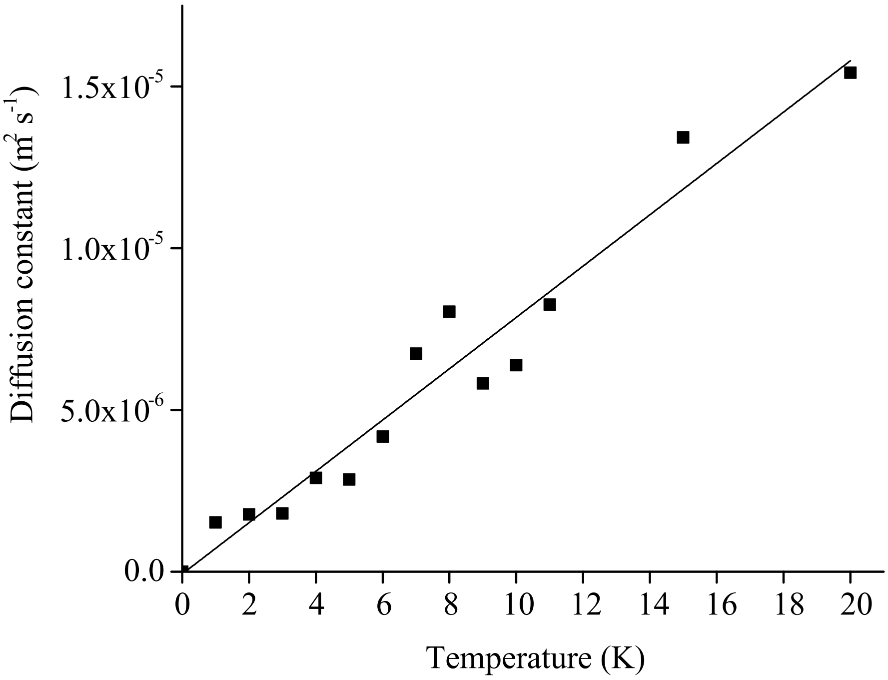

FIG. 4: Low-temperature charge diffusion constant as a function of temperature, satisfying Eq. (15).

temperature) and hence the polaron can crawl less easily along the rings.

For charges, the high temperature behaviour of the diffusion coefficient becomes almost temperature independent above ca. 500 K, indicating a decrease in the charge mobility with increasing temperature. For $T \gtrsim 300$ K, we find that $\mu \sim 2 \times 10^4/T$ cm^2/Vs. We attribute this observation of a decreasing mobility to the localization length of the quasi-extended states decreasing as $T^{-1/3}$, and thus ballistic transport in these extended states is inhibited. (This is in contrast to what is expected in the condensed phase, where disorder is frozen and the localization lengths are temperature independent.[20])

V. CONCLUSIONS

In this work we have studied the motion of a doped charge in a poly(para-phenylene) chain in solution subject to Brownian fluctuations, which cause rotational motion of the phenylene rings. The instantaneous torsional fluctuations cause Anderson localization of the charge wavefunction, with the lower-energy spectrum being composed of local ground states and the higher-energy spectrum being composed of quasi-extended states. At low temperatures, additional charge localization occurs via torsional relaxation, but since the polaron self-trapped binding energy from torsional modes is relatively small (~ 260 K), this is not an important effect at room temperature.

The dynamical torsional fluctuations lead to two distinct modes of motion of the charge: adiabatic and non-adiabatic. Adiabatic motion is a 'crawling' motion of the polaron along the polymer chain while the charge remains in its local ground state. Non-adiabatic motion is a rapid 'hopping' motion as the charge is excited into higher energy quasi-extended states and travels ballistically along the chain before relaxing into a local ground state. The adiabatic motion dominates at low temperatures, and exhibits a linear temperature dependence and thus a constant zero-field charge mobility. Non-adiabatic motion begins to dominate as the temperature is increased, where the charge is thermally excited into higher energy states. At high temperatures the diffusion constant becomes almost temperature independent, indicating a decrease in the charge mobility with increasing temperature, which we attribute to the temperature dependence of the polaron localization length.

This research is thus a natural extension of the previous work by Albu and Yaron, who studied a similar system considering only adiabatic motion.[4] It also makes a link to Fornari and Troisi[5] who considered non-adiabatic transitions in the condensed phase via the FGR formalism. (A direct comparison of mobilities to ref[5] is not meaningful, however, because our calculated mobility is the curvilinear mobility along a chain in solution, not the three-dimensional mobility in the solid state.)

This work is also comparative to that done on exciton dynamics[11]. Notable differences in the dynamics of charges and excitons arise partially due to the charge-polaron binding energy, which is about a sixth of that of the exciton-polaron binding energy. Consequently, non-adiabatic motion occurs at significantly lower temperatures for charges than it does for excitons. The high temperature behaviour also differs; for excitons, in the temperature range analysed, there is a continuous increase of the diffusion constant with temperature, however for charges, the diffusion constant is shown to level off at high temperatures.

Obvious extensions to this work include a treatment of the torsional and vibrational degrees of freedom on an equal footing, and a full time-dependent solution of the charge Schrödinger equation. These extensions, however, require a full quantum mechanical treatment of the problem because first, treating the high frequency C-C vibrations classically causes unphysical self-localization[17] and second, the Ehrenfest approximation fails to properly treat relaxation processes. Finally, extensions to the condensed phase are necessary to predict the charge mobilities in polymer devices.

VI. APPENDIX: THE ROLE OF THE TIME STEP, Δt

Qualitative insight into the role of the time step, Δt, on the charge dynamics can be obtained by considering the Landau-Zener problem.[21] Consider two localized, diabatic states $|\phi_A\rangle$ and $|\phi_B\rangle$, which might correspond to two localized charge states on the chain. The Landau-Zener Hamiltonian is given by

$$\begin{pmatrix} \alpha t & V \\ V & -\alpha t \end{pmatrix},$$

where the off-diagonal elements are the time independent coupling of the two states. If the system is prepared in the diabatic state $|\phi_A\rangle$ at $t \to -\infty$, then the probability, P_B, that it evolves on the instantaneous adiabatic surface, i.e., that there is a transition to the other diabatic state $|\phi_B\rangle$ as $t \to +\infty$, is

$$P_B = 1 - \exp\left(-\frac{\pi V^2}{\alpha\hbar}\right). \qquad (16)$$

For there to be a transition to the other instantaneous adiabatic surface - and hence for the system to remain in its original diabatic state, $|\phi_A\rangle$ - phase coherence in the time-evolving state vector must develop between the two instantaneous eigenstates. Now, suppose that at each time step, Δt, the time-evolving state vector is projected onto the instantaneous eigenstate with the largest overlap. As $\Delta t \to 0$ this projection must always be to the lower energy (initial) instantaneous eigenstate, i.e., the system evolves adiabatically and diabatic transitions from $|\phi_A\rangle$ to $|\phi_B\rangle$ are favoured.

In the context of our simulation we deduce that as Δt is decreased the charge is more likely to undergo transitions between different ‘diabatic’ states and thus increase its mobility. This expectation is confirmed by Fig. 5, which shows that the diffusion constant begins to increase sharply at higher temperatures for very small time steps.

For the temperature ranges modelled in this work, our chosen time step of $\Delta t = 10^{-14}$ s is in the window of time steps which is small enough to ensure accurate Brownian dynamics[15],

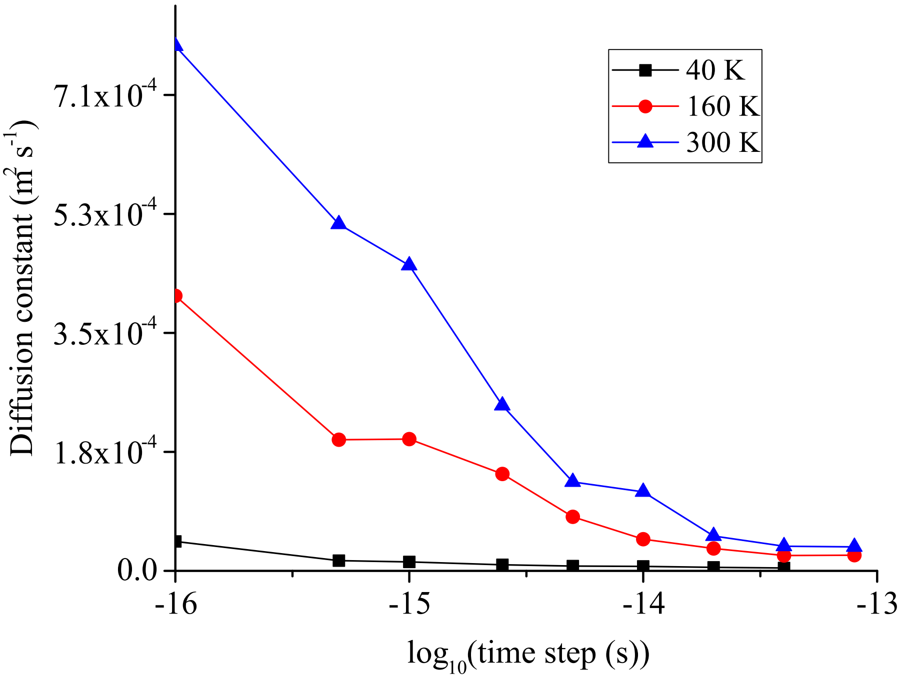

FIG. 5: The charge diffusion constant as a function of the simulation step size, Δt, for different temperatures.

i.e., $\gamma \Delta t << 1$ (where $\gamma = 10^{12}$ s^{-1}), but large enough to avoid the loss of phase coherence and spurious diabatic transitions.

Corresponding author Email address: william.barford@chem.ox.ac.uk

VII. REFERENCES

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[1] P. Prins, F. C. Grozema, and L. D. A. Siebbeles, *J. Phys. Chem. B*, 2006, **110**, 14659.

[2] M. Hultell and S. Stafström, *Phys. Rev. B*, 2007, **75**, 104304.

[3] M. Hultell and S. Stafström, *Phys. Rev. B*, 2009, **79**, 014302.

[4] N. M. Albu and D. J. Yaron, *J. Chem. Phys.*, 2013, **138**, 224902.

[5] R. P. Fornari and A. Troisi, *Phys. Chem. Chem. Phys*, 2014, **16**, 9997.

[6] A. V. Malyshev and V. A. Malyshev, V. A, *Phys. Rev. B*, 2001, **63**, 195111.

[7] D. V. Makhov and W. Barford, *Phys. Rev. B*, 2010, **81**, 165201.

[8] W. Barford and D. Trembath, *Phys. Rev. B*, 2009, **80**, 165418.

[9] H. Ma, T. Qin, and A. Troisi, *J. Chem. Theory Comp.*, 2014, **10**, 1272.

[10] T. Qin and A. Troisi, *J. Am. Chem. Soc.*, 2013, **135**, 11247.

[11] O. R. Tozer and W. Barford, W., *J. Chem. Phys.*, 2015, **143**, 084102.

[12] N. M. Albu and D. J. Yaron, *J. Phys. Chem. C*, 2013, **117**, 12299.

[13] W. Barford, Electronic and Optical Properties of Conjugated Polymers, Oxford University Press, Oxford, 2013.

[14] R. Kubo, *Rep. Prog. Phys.*, 1966, **29**, 255.

[15] W. F. van Gunsteren and H. J. C. Berendsen, *Molecular Physics*, 1982, **45**, 637.

[16] A. P. Horsfield, D. R. Bowler, A. J. Fisher, T. N. Todorov, and C. G. Sánchez, *J. Phys.: Condens. Mat.*, 2004, **16**, 8251.

[17] O. R. Tozer and W. Barford, *Phys. Rev. B*, 2014, **89**, 155434.

[18] P. W. Anderson, *Phys. Rev.*, 1958, **109**, 1492.

[19] B. Kramer and A. MacKinnon, *Rep. Prog. Phys.*, 1993, **56**, 1469.

[20] N. F. Mott and E. A. Davis, Electronic Processes in Non-crystalline Materials, Oxford University Press, Oxford, 1979.

[21] A. Nitzan, Chemical Dynamics in Condensed Phases, Oxford University Press, Oxford, 2006.