



Supersonic quasi-particles dynamics in organic semiconductors

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ABSTRACT

We investigate the dynamics of charge-carriers schemes on high external electric fields in organic semiconductors. Specifically, the critical field strength needed for the transition from subsonic to supersonic regime was determined for solitons and polarons in conjugated polymers, for both *trans*- and *cis*-symmetry. Also, the collision between quasi-particles and impurities, at supersonic regime, is investigated. For this purpose it is used a modified Su–Schrieffer–Heeger hamiltonian model in the scope of an Ehrenfest molecular dynamics. The results provide useful information regarding the behavior of the conductivity of conducting polymers measured for different electric fields and bearing different types of impurities.

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1. Introduction

The use of organic semiconductors in optoelectronic devices has attracted the attention of both academia and industry to this new class of materials in the last 20 years [1]. Competitive organic field effect transistors (OFET), organic light emitting diodes (OLEDs) and organic photovoltaic cells (OPVs) have been demonstrated with satisfactory efficiency and lifetime [2–8]. In particular, organic photovoltaic devices have been receiving special attention due to its potential for generating clean energy at a lower cost. Even though that the understanding of the mechanism of charge transport in these materials is crucial to the development of efficient devices [1], a better phenomenological description of such phenomena is still lacking. Here, the dynamics of polarons under large external electric field was studied using a modified Su–Schrieffer–Heeger (SSH) model. It has been shown that in the presence of an electric field, the polaron has a saturation speed equal to 1.5 \AA/fs , just below the speed of sound, and that this quasi-particle is stable under fields up to 6 mV/\AA [9]. On the other hand, using a similar approach, another study performed by Stafström and collaborators [10] suggests that the process of polaron dissociation occurs in two steps: Firstly, at a critical field strength of 0.14 mV/\AA , the acoustic mode decouples from the charge-carrier. The characteristic profile of charge distribution of a polaron is maintained, and the quasi-particle is able to reach four times the speed of sound. Second, at another critical field strength of 2.6 mV/\AA , both acoustic and optical mode decouple from the charge and the polaron loses its identity. Also, the maximum speed that the charge-carrier can reach has been shown to be directly related to the way which the electric field is

applied, without changing the critical field strengths [11]. The charge-carrier mobility is directly related to its speed and the way it responds to and electric field. However, the existence of these quasi-particles is closely related to the presence of impurities in the material. The impurities provide the symmetry breaking needed to the the creation of solitons, polarons and bipolarons. On the other hand, impurities acts as charge traps, disrupting the charge transport. In this Letter, we studied the dynamics of charge carriers at the supersonic regime in conjugated polymers bearing impurities. Our methodology is based on an Ehrenfest molecular dynamics applied to a modified tight-binding Hamiltonian of the SSH type, where the effects of impurities and the presence of an external electric field are included in the model. Using this model, we estimate the critical field strength needed to achieve the supersonic regime for both solitons and polarons in *cis*- and *trans*-symmetry. Besides, the collision process between quasi-particles at supersonic speed and impurities is investigated, leading to the conclusion that even though solitons have a smaller terminal speed compared to polarons, they have a larger probability to cross the impurity barrier.

2. Methodology

The methodology adopted here is based on an Ehrenfest molecular dynamics simulation. A tight-binding approach with lattice relaxation taken into account in first-order approximation is used in conjunction with a SSH-type Hamiltonian, modified to include the effects of impurities and of an external electric field. In the numerical simulations performed here, the electrons are taken into account by solving the time-dependent Schrödinger equation, whereas the lattice is described classically. The SSH Hamiltonian [12] is given by:

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$$H = -\sum_{n,s} \left(t_{n,n+1} C_{n+1,s}^\dagger C_{n,s} + H.c \right) + \sum_n \frac{K}{2} y_n^2 + \sum_n \frac{p_n^2}{2M} + V_j C_{j,s}^\dagger C_{j,s}, \quad (1)$$

where $C_{n,s}^\dagger$ ($C_{n,s}$) is the creation (annihilation) operator of a π -electron with spin s at the n th lattice site; K is the harmonic constant due to the σ bonds. M is the mass of a CH group and $y_n \equiv u_{n+1} - u_n$, where u_n is the lattice displacement of the atom at n th site along the chain. The conjugated momentum of u_n is p_n . The hopping integral is given by $t_{n,n+1} = \exp(-i\gamma\hat{A}) \{ [1 + (-1)^n \delta_0] (t_0 - \alpha y_n) \}$, being t_0 the hopping integral between the nearest-neighbor sites in the undimerized chain, α is the electron–phonon coupling, and δ_0 is the Brazovskii–Kirova symmetry-breaking term. V_j is the strength of an impurity, which is located in j th site, $\gamma \equiv ea/(hc)$, where e is the absolute value of the electronic charge, a is the lattice constant, and c is speed of light. The relation between the time-dependent vector potential A and the uniform electric field E is given by $E = -(1/c)\dot{A}$. The parameters used here are $t_0 = 2.5$ eV, $M = 1349.14$ eV fs²/Å², $K = 21$ eV Å⁻², $\delta_0 = 0.05$, $a = 1.22$ Å, $\alpha = 4.1$ eV Å⁻¹ and a bare optical phonon energy $\hbar\omega_Q = \sqrt{4K/M} = 0.16$ eV. These values have provided good descriptions and the results obtained using them are expected to be valid for conjugated polymers in general [13,14]. In order to solve the problem numerically, we must first obtain an initial solution for the polymer chains, i.e., we must obtain a stationary state, fully self-consistent with the degrees of freedom for electrons and lattice. The time evolution of the lattice configuration is then determined by the equations of motion. The equations of motion for the electronic wave function $\psi_{k,s}$ is the solution of the time-dependent Schrödinger equation that have the following form:

$$i\hbar\dot{\psi}_{k,s}(n,t) = -t_{n,n+1}\psi_{k,s}(n+1,t) - t_{n-1,n}^*\psi_{k,s}(n-1,t) + V_j\delta_{n,j}\psi_{k,s}(n,t). \quad (2)$$

where k labels the electronic energy state and s its spin. The equation of motion of the lattice is determined within a classical approach by means of Euler–Lagrange equations:

$$\frac{d}{dt} \left(\frac{\partial(L)}{\partial \dot{u}_n} \right) - \frac{\partial(L)}{\partial u_n} = 0 \quad (3)$$

where $\langle L \rangle = \langle T \rangle - \langle V \rangle$. Eq. (4) leads to

$$M\ddot{u}_n = F_n(t), \quad (4)$$

where

$$F_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[B_{n,n+1} - B_{n-1,n} + B_{n+1,n} - B_{n,n-1}], \quad (5)$$

with $B_{n,n'} = \sum_{k,s} \psi_{k,s}^*(n,t)\psi_{k,s}(n',t)$, being the term that couples the electronic and lattice problems. The primed summation represents a sum over the occupied states only. To perform the dynamics, an initial self-consistent state is prepared solving Eqs. (3) and (5) simultaneously. Periodic boundary conditions are used. The initial state is taken in equilibrium ($E = 0$). Therefore, we have $\dot{u}_n = 0$ for all n in the initial state. The equations of motion (2) and (4) are solved by discretizing the time variable with a step Δt . This time step is chosen so that the change of $u_i(t)$ and $\dot{A}(t)$ during this interval is always very small on the electronic scale. Eq. 2 is integrated by introducing single-electron eigenstates at each step. Therefore, the solutions of the time-dependent equations can be put in the form,

$$\psi_{k,s}(n, t_{j+1}) = \sum_l \left[\sum_m \phi_{l,s}^*(m, t_j) \psi_{k,s}(m, t_j) \right] \times \exp \left(-i \frac{\epsilon_l \Delta t}{\hbar} \right) \phi_{l,s}(n, t_j), \quad (6)$$

where $\{\phi_l\}$ and $\{\epsilon_l\}$ are the eigenfunctions and the eigenvalues of the single-electron hamiltonian at a given time t_j . The lattice equations are written as

$$u_i(t_{j+1}) = u_i(t_j) + \dot{u}_i(t_j) \Delta t \quad (7)$$

and

$$\dot{u}_i(t_{j+1}) = \dot{u}_i(t_j) + \frac{F_i(t_j)}{M} \Delta t. \quad (8)$$

Hence, the electronic wave functions and displacement coordinates at the $j+1$ th time step are obtained from the j th time step. For all simulations, 200-site chains with periodic boundary conditions are used. The behavior of the charge-carrier is analyzed by evaluating the temporal evolution of the charge density and the speed of the quasi-particle of interest as it moves along the polymer chain. The charge carrier position is defined by its center of charge, i.e. the weighted average location of the carrier charge on the polymer. Their speed is just the position variation over time. The dimerized configuration generates a bond length variable y of alternating sign. To provide a good visualization of the results, it is defined order parameters for the charge density, $\bar{\rho}_n(t)$, as follows: $\bar{\rho}_n(t) = 1 - [\rho_{n-1}(t) + 2\rho_n(t) + \rho_{n+1}(t)]/4$. The center position of the charge carrier $\langle p \rangle(t)$ at a given time t , is calculated from a cyclic mean value of the charge density:

$$\langle p \rangle(t) = \frac{N}{2\pi} \arg \left\{ \left[\sum_{n=1}^N \bar{\rho}_n(t) e^{i(2\pi/N)n} \right] \right\}. \quad (9)$$

3. Results

To characterize the transition from subsonic to supersonic speed, the polymer chain is subjected to different external electric field regimes. Figure 1 shows quasi-particles speed as a function of the strength of the applied electric field. In the Figure 1a, it can be seen the transition behavior for polarons in both symmetries, *cis* and *trans*, whereas Figure 1b presents the speeds for solitons. From the results displayed in Figure 1a it is possible to conclude that, for the polaron in both symmetries, the value of the critical field strength needed to reach supersonic speed is between 0.135 and 0.140 mV/Å. A similar magnitude was reported by Stafström et al. for a polaron in a *trans*-PA molecule [10], knowing that the speed of sound is 0.15 Å/fs in polyacetylene. Due to fact that the soliton have effective mass of order of 6 m_e , where m_e is the electron mass, while the polaron effective mass is approximately 1 m_e , the soliton is less accelerated than the polaron for all field strengths, as can be noted in Figure 1b. Thus, the critical field strength for the transition from subsonic to supersonic speed is larger in the case of solitons. In the simulations performed here, these field value is approximately 0.250 mV/Å. Also, at low field strengths, it is possible to see in Figure 1 an approximately discontinuous change from speed slightly below the sound speed to a supersonic speed for all charge carriers. For fields strengths higher than 0.25 mV/Å, the speed increases at a slower pace with the field. The lattice displacements associated with the charge carriers, i.e., the phonons produced by the polaron movement through the lattice, in both symmetries, can no longer follow the electronic motion and therefore are decoupled from the charge. This effect reduces their effective mass, which explains the increase in speed. Also, the polaron speed in *trans*-polyacetylene (tPA) is larger than in *cis*-polyacetylene (cPA), as seen in Figure 1a. This fact can be attributed to the high instability of polaron in tPA chains [15]. When the charge carriers begin to move upon application of the external electric field, acoustic phonons are emitted in both directions. Phonons that move in the forward direction produce the sound wave that moves at approximately at the speed of sound.

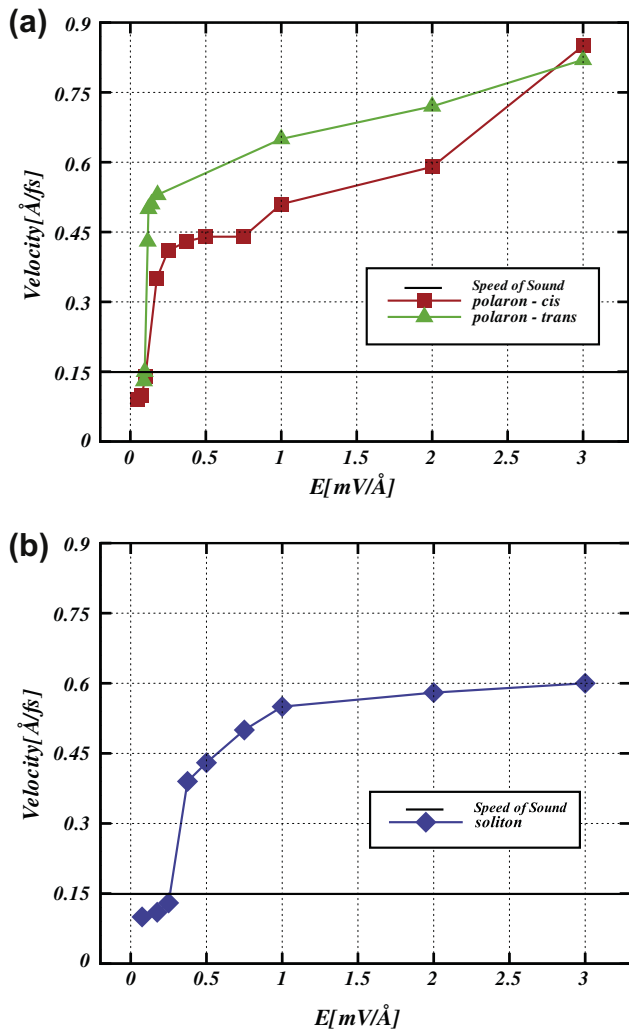


Figure 1. Charge carrier speed as a function of the strength of the applied electric field.

In the regime of higher electric field, charge carriers have enough energy to overcome the potential barrier associated to the phase transition and keep accelerating until the supersonic speed is reached. In this regime, optical phonons are emitted by the charge-carriers. The transition state from the subsonic to the supersonic regime can be seen as a transition from the acoustic to the optical vibration mode of the lattice. Table 1 presents the terminal speed and the critical field strength needed for the transition from subsonic to supersonic regime for solitons and polarons (*trans*- and *cis*-symmetry). It can be noted that the terminal speed of a polaron in *trans*-symmetry is higher when compared with a polaron in *cis*-symmetry. The dimerization in *trans*-symmetry conjugated polymers tends to be stronger than the *cis*-symmetry. On the other hand, the increase in dimerization leads to an increase in the charge localization, generating a decrease on charge carrier speed. Also, for electric field intensity greater than $2 \text{ mV}/\text{\AA}$ the ob-

Table 1

Critical field ($\text{mV}/\text{\AA}$), terminal speed ($\text{\AA}/\text{fs}$) and the ratio (R) between the terminal speed and the speed of sound.

Quasi-particles	Critical fields	Terminal speed	R
Soliton	0.253	0.56	~ 3.9
Polaron <i>cis</i>	0.137	0.59	~ 3.9
Polaron <i>trans</i>	0.137	0.72	~ 4.8

served charge carriers are not typical, i.e. the charge profile of those carriers deviates from what is observed on typical polarons and solitons. In this sense, for fields in the order of $3 \text{ mV}/\text{\AA}$, the charge is almost decoupled from the lattice and the main chain symmetry will barely affect the charge carriers. We also investigate the effect of a collision of a supersonic soliton and an impurity. In Figure 2, the collision process between a positively charged soliton and an impurity is depicted. The impurity has intensity of $7.5 \times 10^{-2} \text{ eV}$ and is placed on the site 100 in the lattice. The system is subjected to an electric field of $1 \text{ mV}/\text{\AA}$. For this electric field strength, the soliton reaches a supersonic speed $0.46 \text{ \AA}/\text{fs}$ and transposes easily the impurity. The situation is quite different when a polaron interacts with an impurity. It is found that, for the same values of electric field and impurity, when a polaron is taken into account, the propagation falls dramatically. In contrast, for systems with solitons as charge carriers there was no decrease in the carrier propagation, as observed in Figure 2. Figure 3 shows a collision process between a positive polaron with an impurity. In the moment of the collision, the speed of the polaron is $0.55 \text{ \AA}/\text{fs}$ (supersonic speed), that is approximately four times the sound speed in the material. After 200 fs of simulation, the interaction between the polaron and the impurity starts to spread out charge across the lattice, as can be seen in Figure 3. During the collision process, the polaron speed is reduced due to the interaction with the impurity and ends up being trapped. Different from what is observed for a polaron, a soliton can cross the barrier despite colliding with a speed slightly below the speed of the polaron, $0.41 \text{ \AA}/\text{fs}$. This is because,

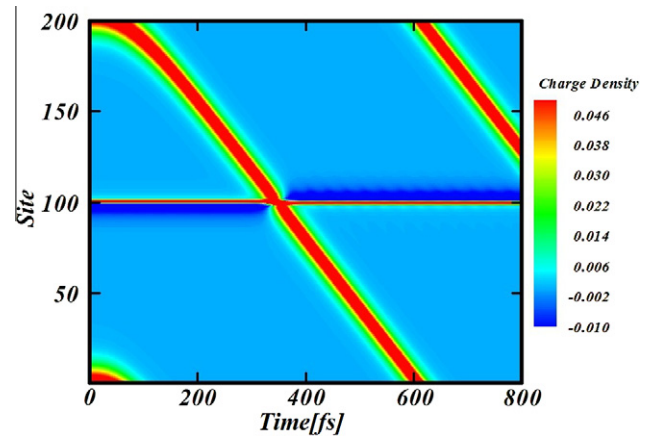


Figure 2. Collision process between a supersonic soliton and an impurity.

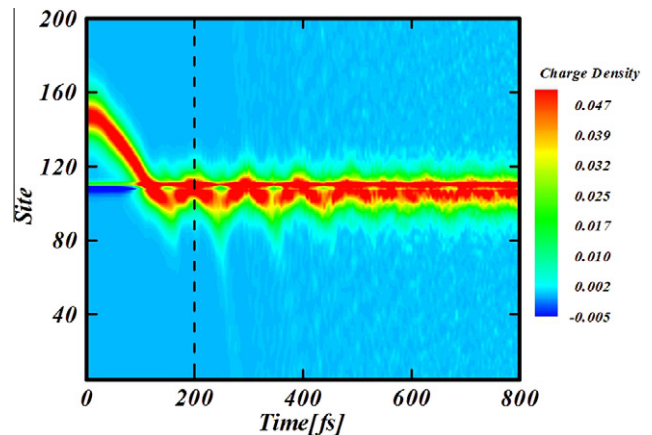


Figure 3. Collision process between a polaron and an impurity.

even the speed of soliton being lower, it has an effective mass larger than the effective mass of a polaron and thus larger inertia.

4. Conclusions

We studied the dynamics of charge carriers at the supersonic regime in conjugated polymers bearing impurities. Regarding to the charge-carrier speed, the critical field strength needed for the transition from subsonic to supersonic regime was determined for solitons and polarons. In the case of polarons, we have considered both *cis* and *trans* symmetries. The results obtained here are in agreement with earlier theoretical studies for the case of *trans* symmetry. The novel result is the determination of critical fields for both solitons and polarons in *trans* symmetry. The obtained critical field strength for polarons in *cis* symmetry is about the same as in the case of *trans* symmetry, although the terminal speed reached is higher in the latter case. In the case of solitons, our simulations show that the transition from subsonic to supersonic regime occurs for critical field strength that is about twice the one needed in the case of polarons. The collision process between a quasi-particles at supersonic speed and impurities were investigated. Our results show that even though solitons have a smaller terminal speed compared to polarons, their probability to cross the impurity barrier is higher. This leads to the conclusion that, in the simulated regime, when the charge carriers are solitons, the material conductivity remains unchanged. However, if the charge-carriers are polarons, the material conductivity should falls

dramatically. The understanding of the effects considered in this Letter can shed light on the transport mechanisms in conducting polymers and how to optimize it varying the electric field strength and the type of impurities used to dope these materials.

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References

- [1] V. Coropceanu, J. Cornil, D.A. da Silva, Y. Olivier, R. Silbey, J.L. Bredas, *Chem. Rev.* 107 (2007) 926.
- [2] G.R. Whittell, U.S. Schubert, M.D. Hager, I. Manners, *Nat. Mater.* 10 (2011) 176.
- [3] Y. Yuan et al., *Nat. Mater.* 10 (2011) 296.
- [4] M.G. Kim, M.G. Kanatzidis, A. Facchetti, T.J. Marks, *Nat. Mater.* 10 (2011) 382.
- [5] D. Li, Y. Le, X.Y. Hou, J.F. Chen, Z.G. Shen, *Synth. Met.* 161 (2011) 1270.
- [6] S. Chen, G. Tan, W.Y. Wong, H.S. Kwok, *Adv. Funct. Mater.* 21 (2011) 3785.
- [7] Y. Sun et al., *Adv. Funct. Mater.* 21 (2011) 1881.
- [8] S. Stafström, *Chem. Soc. Rev.* 39 (2010) 2484.
- [9] D.M. Basko, E.M. Conwell, *Phys. Rev. Lett.* 88 (2002) 056401.
- [10] A.A. Johansson, S. Stafström, *Phys. Rev. B* 69 (2004) 235205.
- [11] X. Liu, K. Gao, J. Fu, Y. Li, J. Wei, S. Xie, *Phys. Rev. B* 74 (2006) 172301.
- [12] W.P. Su, J.R. Schrieffer, A.J. Heeger, *Phys. Rev. B* 22 (1980) 2099.
- [13] L.A. Ribeiro, P.H. de Oliveira Neto, W.F. da Cunha, L.F. Roncaratti, R. Gargano, D.A.S. Filho, *J. Chem. Phys.* 135 (2011) 224901.
- [14] P.H. de Oliveira Neto, W.F. da Cunha, G.M. e Silva, *Europhys. Lett.* 88 (2009) 67006.
- [15] W.F. da Cunha, P.H. de Oliveira Neto, R. Gargano, G.M. e Silva, *Int. J. Quan. Chem.* 108 (2008) 2448.