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On the electron transport in polydiacetylene crystals and derivatives

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Abstract – We provide here a theory to account for the thirty-year-old outstanding experimental results by Donovan and Wilson on the electron transport in polydiacetylene (PDA) single crystals. Both supersonic and subsonic velocities are described. In the former case we predict that the velocity is field independent for several decades of the field strength in accordance with experimental results. The results offer a novel form of electron transport in addition to the previously known form in (trans)polyacetylene and other conjugated polymers.

In this letter we discuss the possibility of subsonic and supersonic electron surfing on *acoustic* lattice solitons thus providing a theory to support the experimental results obtained long ago by Donovan and Wilson on polydiacetylene (PDA) single crystals and some derivatives [1–4]. The results offer a novel form of electron transport in addition to the Heeger discovery in (trans)polyacetylene (tPA) and other conjugated polymers [5].

PDA crystals are composed of parallel long π conjugated carbon chains spaced apart by inert side groups. The interchain distance is sufficiently large so that π electron transfer between chains is not possible. Thus, they form a perfect scenario for the investigation of one-dimensional (1d) electron transport (figs. 1, 2) [6]. Experiments by Wilson and collaborators in the 1980s [1–4] were on the transient photo-conduction, over 10 time decades, of currents induced by light pulses, of picoseconds to seconds. The photo-generation efficiency is linear in the field, as established by the "cuts" experiments on PDATS [1] and the "electronic walls" experiment in PDADCH [4]. The velocity is independent of the applied field over several orders of magnitude of the field. The initial current induced by the light pulse, *i.e.*, the photo-efficiency of the generation multiplied by the velocity, is linear in the field. The low field mobility is ultra-high, *i.e.*, higher than in any conventional semiconductor. Wilson [7] assumed that an electron self-traps in the acoustic distortion that it creates in one such π conjugated carbon chain and travels, as a localized state, along the carbon backbone. Dissipation was shown to be very weak, so the smallest field gives rise to a virtually constant velocity just below the sound velocity. Below we show that replacing the harmonic interactions in the lattice Hamiltonian [7] by Morse interactions, the self-trapping (polaron) effect is overwhelmed by a soliton-assisted process thus offering supersonic as well as subsonic electron transport.

Since the experiments in the 1980s [1–4] few transport experiments have been performed. There are two problems. First, it was difficult, in the 1980s experiments, to inject carriers from electrodes into the PDA. Also, unlike the standard conducting polymers, PDA cannot be chemically doped to create carriers. Indeed, these perfect 1d chains provide the electron high mobility; but the perfection does not allow for doping. Second, due to the high perfection of the crystals, a kind of "queuing" is postulated to occur. Consider an electron on a particular chain to be trapped at some defect or chain end. Electrons travelling on adjacent chains then queue up behind the trapped

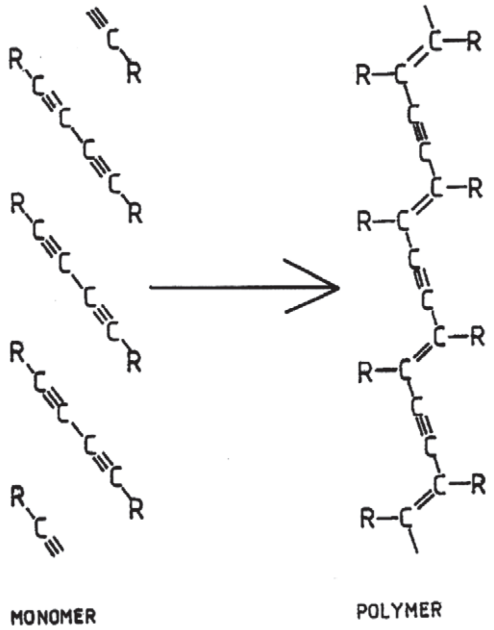

Fig. 1: Solid-state polymerisation of PDA: one-dimensional C chain, one electron per C atom, 4 C per unit cell, 4 bands, 2 full, 2 empty and 2 eV gap semiconductor [6].

Fig. 2: (Colour on-line) Electron microscope lattice image of a PDA crystal. Horizontal interline spacing: 1.2 nm [6].

charge provided the chains are within a Coulomb radius of the first chain. Such electrons cannot escape the queue by perpendicular diffusion, as would occur in a 2d or 3d material. Queuing thus suppresses the unipolar current. Thus, though the perfect 1d chains allow for high electron mobility they also give rise to the disruptive queuing phenomena. Suppose electrons and holes to be travelling in opposite directions on chains. The electron hole collisions on chains within a Coulomb radius will cause electron-hole binding, *i.e.*, exciton formation. The neutral interchain exciton does not contribute current, but remains with a long lifetime, causing further bipolar current disruption. This bipolar phenomenon has been experimentally observed [8]. Its existence leads to the expectation of the unipolar queuing phenomenon above. Donovan and Wilson found that in the crystalline toluene sulphonate derivative of PDA, namely PDATS photo-carriers travelled up to one mm at a constant velocity over four decades of the field, in the range $10^2 < \tilde{E} < 10^6\,\mathrm{Vm}^{-1}$. For later convenience we denote with a tilde the dimensional field. The velocity of 2 km/s was subsonic, just below the estimated sound velocity of 3.6 km/s. On the other hand in PDADCH (containing di-N-carbazolyl) there was found supersonic electron velocities of ca. 5 km/s in the range $4 \times 10^2 < \tilde{E} < 4 \times 10^5\,\mathrm{Vm}^{-1}$. It is tempting to associate the higher experimental velocity in PDADCH with the supersonic case, in contrast to the lower experimental velocity in PDATS. However, some caution is necessary. The authors pointed out in [4] that the experimental velocity would be reduced by a factor of two if both signs of carrier were equally mobile. The latter is not known in PDADCH. Also, the value of the sound velocity along the polymer chain is not well established. It was estimated [9] to be 3.6×10^3 from determinations of elastic moduli found in hydrostatic pressure experiments on PDATS. The moduli are highly anisotropic. There are no such experiments on PDADCH.

To theoretically understand the lattice dynamics behavior of the crystal we assume that along the lattice the units interact with Morse potentials $V(r) = D\left(e^{-2br} - 2e^{-br}\right)$. Here D denotes the potential well depth and b is the stiffness constant of the "springs"; r stands for relative displacements of lattice units, otherwise denoted by $(x_n - x_{n-1})/\sigma$, with σ the equilibrium inter-unit distance. The electrons follow the Schrödinger evolution equation and their interaction with the lattice is considered in the tight-binding approximation. Accordingly, the Hamiltonian of the system is [10,11] $H = H_{lat} + H_{el}$ with

$$H_{lat} = \sum_n \left\{ \frac{p_n^2}{2M} + D\left[e^{-2b(x_n - x_{n-1} - \sigma)} - 2e^{-b(x_n - x_{n-1} - \sigma)}\right] \right\}, \quad (1)$$

$$H_{el} = \sum_n E_n(q_n)\, c_n c_n^* - \sum_n V_{n,n-1}(q_n)\left(c_n^* c_{n-1} + c_n c_{n-1}^*\right), \quad (2)$$

$$E_n = E_n^0 + \chi_0 q_n + \chi_1 (q_{n+1} - q_{n-1}), \quad (3)$$

$$V_{n,n-1} = V_0 e^{-\hat{\alpha}(q_n - q_{n-1})}, \quad (4)$$

with $q_n = b(x_n - n\sigma)$. $|c_n|^2$ denotes the electron probability density at lattice site n. Note that here we only consider acoustic lattice excitations. For simplicity we assume that the values of E_n^0, χ_0 and χ_1 can be set to zero, in a first approximation. Following Slater and others [12,13] the $V_{n,n-1}$ terms are the hopping transfer matrix elements or overlapping integrals. V_0 and $\hat{\alpha}$ account for the electron-lattice interaction. For universality of our argument we choose $1/b$ as unit of length, $1/\omega_M$ as time unit (ω_M is the linear oscillation frequency of the Morse potential), $2D$ as energy unit for the lattice and $(h/2\pi)\,\omega_M$ as energy unit for the electron. Thus, we set $V = V_0/2D$ $\alpha = \hat{\alpha}/b$, and $\tau = V_0/(h/2\pi)\,\omega_M$. By Taylor-expanding (4) we recover the standard linear form used in textbooks and in refs. [5,14].

Our Hamiltonian (1)–(4), with only longitudinal, acoustic, dispersive, Debye oscillators, embraces the one used by Wilson [7] and the so-called SSH Hamiltonian describing the dynamics of transpolyacetylene [14]. It is covered by a more general description kind of "umbrella" Hamiltonian if on-site, non-dispersive, Einstein oscillators are added, $\chi_1 = 0$. When linearization is done for the dynamics of the longitudinal vibrations, one recovers the so-called Davydov Hamiltonian [15]. Otherwise, restricting the on-site oscillations to the harmonic case, one recovers the so-called Holstein Hamiltonian [16]. Finally, our Hamiltonian (1)–(4) with $\chi_0 > 0$, can also encompass existing models of DNA. Suppose DNA be considered as a staircase whose steps are the base pairs. If the base-pair relative vibrations along the staircase are harmonic, then our Hamiltonian corresponds to that of the DNA model of Peyrard and Bishop [17]. If in addition, such harmonic interactions are modified with an *ad hoc* empirical (nonlinear) prefactor, making it anharmonic, then our Hamiltonian becomes that of the Dauxois, Peyrard and Bishop DNA model [18] yet to be used to account for transport. As the above comments on DNA refer to mostly formal aspects in the mathematical modelling, it seems pertinent to recall the insightful discussion offered by Conwell [19] about the role of polarons for charge transfer particularly when in solution. Finally, including the interactions with the electron dynamics such kind of "umbrella" Hamiltonian permits a description of all possible cases of physical interest with phonons, breathers and solitons and their corresponding interactions among themselves.

Thus, in view of the above the evolution of the overall system in dimensionless units is given by the equations (incorporating an additional external electric field [20])

$$\frac{\mathrm{d}^2 q_n}{\mathrm{d}t^2} = \left[1 - e^{(q_n - q_{n+1})}\right] e^{(q_n - q_{n+1})} - \left[1 - e^{(q_{n-1} - q_n)}\right] e^{(q_{n-1} - q_n)} + 2\alpha V \left[\Re\left(c_{n+1} c_n^*\right) e^{\alpha(q_n - q_{n+1})} - \Re\left(c_n c_{n-1}^*\right) e^{\alpha(q_{n-1} - q_n)}\right], \tag{5}$$

$$\frac{\mathrm{d}c_n}{\mathrm{d}t} = i\tau\left[c_{n+1} e^{\alpha(q_n - q_{n+1})} + c_{n-1} e^{\alpha(q_{n-1} - q_n)}\right] + i\left(n - n_{el}\right) E c_n \tag{6}$$

together with periodic boundary conditions: $q_{N+1} = q_1$ and $\dot{q}_{N+1} = \dot{q}_1$. $E = \tilde{E}\left(h/2\pi\right)\omega_M/\sigma e$ with $\tilde{E}$ the dimensional field in Vm^{-1} and e denoting the electron charge; $\Re$ denotes the real part.

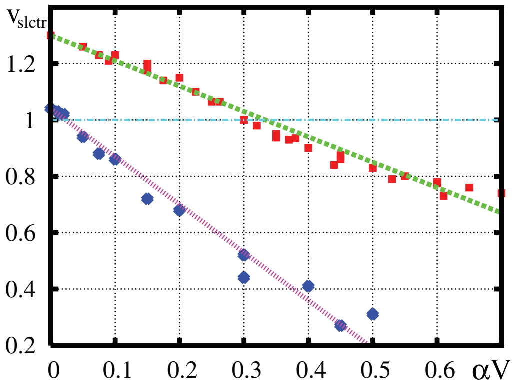

Fig. 3: (Colour on-line) Solectron velocity *vs.* αV, for $\kappa = 0.5$ with initial $v_{sol} = 1.04$ (pink bottom line) and for $\kappa = 1.35$ with $v_{sol} = 1.3$ (green upper line). Dots are computer simulation values and straight lines approximate fits, $v_{slctr} = 1.3 - 0.9\alpha V$ (upper line) and $v_{slctr} = 1.04 - 1.7\alpha V$ (lower line), respectively.

For the expected soliton solution we take as initial condition $e^{3(q_n - q_{n+1})} = 1 + \frac{\beta^2}{\cosh^2(\kappa n - \beta t)}(t = 0)$ with the corresponding albeit involved formula for its velocity; $\beta = \sinh(\kappa)$ and κ in units $1/\sigma$ is the mid-height inverse width of the soliton. For simplicity, at $t = 0$ we take the electron probability density (normalized to unity $\sum_n |c_n|^2 = 1$) as a Gaussian distribution, centered at site n_{el}, with a width σ_{el}, which is approximately that of the chosen soliton initial condition. For illustration we take $\sigma_{el} = 3$ and $\tau = 10$ in all our computations [10]. At this point it appears worth recalling the detailed discussion on the difference existing between a semiclassical and a fully quantum approach in estimating the time scale for polaron formation [21]. In our case here the soliton is a very small entity just comprising a few lattice sites. Considering even up to ten such sites and a few, three to five, local oscillations, the onset time is about a picosecond. Recall also that lattice solitons (in the absence of added electrons) are always moving with supersonic velocities with direction given by the initial conditions. Solving the equations numerically, with boundary and initial conditions, after a short transient, one observes the formation of a new stationary bound state of soliton with the electron (denoted solectron). The solectron velocity (in units of sound velocity) is estimated as the slope of its trajectory on the space-time (n, t) plot. In our computations we take reasonable advantage of the large mass difference between the electron and the lattice units, the latter are thousand times heavier. This means vibrations in the ultraviolet range for the former and in the far infrared range for the latter.

The results found are displayed in figs. 3, 4 and 5. Figure 3 depicts the solectron velocity *vs.* the compound parameter αV accounting for the electron-lattice interaction. As expected, the latter affects the soliton in a drastic way with, however, supersonic values in a significant range $(0 < \alpha V < 0.3)$. Figure 4 shows the space-time evolution of the electron probability density in the bound state with the soliton in the absence of the electric field. We placed the soliton and the electron at lattice site 100 to rule out boundary effects. This is not a limitation since, wherever the electron is placed along the lattice, the soliton placed in the same or different site is always able to trap it. Note that this is at variance with the standard polaron which forms only in response to the charge after it is

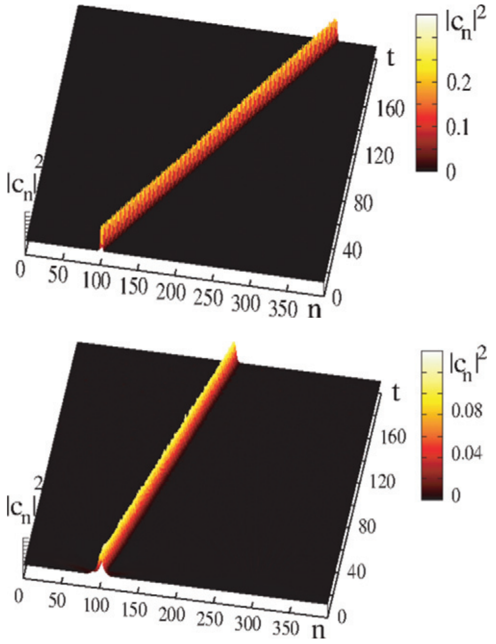

Fig. 4: (Colour on-line) Space-time evolution in a lattice with $N = 400$ of the electron probability density $|c_n|^2$ in the absence of the field, $E = 0$. Upper panel: supersonic case ($\alpha = 1,\ V = 0.1$). Lower panel: subsonic case ($\alpha = 1,\ V = 0.3$).

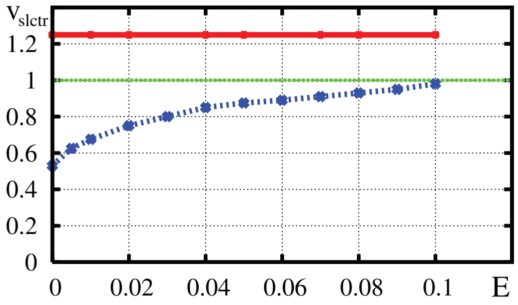

Fig. 5: (Colour on-line) Dimensionless subsonic (lower blue curve) and supersonic (upper red line) solectron velocity *vs.* dimensionless electric field strength. The horizontal green line at the value unity corresponds to the (linear) sound velocity in the system. $E = 0.1$ corresponds to the dimensional $\tilde{E} = 10^6\,\text{Vm}^{-1}$, as defined in the main text.

injected. When the electric field is switched-on we observe in fig. 5 that, on the one hand, there is a domain up to, say, $E = 0.1$ where the drift velocity is field independent for quite a wide range of values of the field strength. On the other hand, in the subsonic case the drift velocity grows with the increasing field reaching saturation at the sound velocity.

Figure 5 also indicates two significant consequences. On the one hand, as the field strength goes down, an ultra-high mobility is expected, in agreement with the above-mentioned experimental results. On the other hand, the electric field appears as a symmetry-breaking left-right agent. Indeed, in general, our model implies that motion is always expected even in the absence of an external electric field, once the soliton is excited. But, on the average as solitons, and hence the solectrons, can move to the left or to the right, no net conduction would be the outcome. Switching on the field breaks the symmetry thus allowing one or the other to be realized. For the subsonic case, the results here presented recover results obtained by Wilson [7], by Ono and Teray [20] and by Gogolin [22,23] when the Morse potential reduces to the harmonic approximation.

Crystal lattice solitons are generally the dominant lattice excitations past the Dulong-Petit plateau in the specific heat, a result confirmed by computation of the *dynamic* structure factor [10]. Needless to say our theory is just a first albeit significant step to account for the findings of Donovan and Wilson [1–4]. Clearly our supersonic lattice soliton is different from the subsonic soliton of the SSH theory [5,14] which originates in the degeneracy of the ground state of their Hamiltonian for tPA.

New experiments seem desirable in order to have a solid ground for further insight into the problem foreseeing potential revolutionary applications. For instance, one can propose to perform injection experiments. Since the 1980s there has been an increased international effort on Organic Light-Emitting Diodes (OLED), in both conducting polymers, and in organic molecular systems. This has led to a greater ability to produce electron- and hole-injecting electrodes, allowing prolific injection. The electron mobility in the OLED is very small, due to their structural disorder. Accordingly, it would be useful to revisit the experiments on PDA of the 1980s, but using the electrode systems of the OLED. It can be also suggested to attempt screening of the Coulomb interaction, in order to diminish effects of the earlier-mentioned queuing. This may be carried out by using a crystal as thin as the Coulomb radius, having a dilute ionic solution in contact with the crystal surface. If the Debye screening length of the solution is less than the Coulomb radius of the PDA, then a considerable reduction of queuing is expected. In particular, the decay of an electron-hole photo-current due to interchain exciton creation has already been observed. The decay rate should diminish on addition of the ionic solution [8]. The ability to achieve prolific injection together with a reduction of queuing should enable us to exploit the high soliton-assisted mobility in PDA and achieve the room temperature super-metal.

Finally, note that our soliton-assisted (solectron) transport theory offers universality. Indeed, besides the application here described to PDA, it can be used for other materials whose stiffness and crystal vibrations permit strong enough compressions capable of exhibiting nonlinear soliton excitations. It also offers the possibility of a mechanical control of electrons at the nano-scale [24].

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