Current without external bias and diode effect in shuttling transport of nanoshafts

K Morawetz$^{1,2,3}$, S Gemming$^1$, R Luschtinetz$^4$, L M Eng$^5$, G Seifert$^4$ and A Kenfack$^2$

$^1$ Forschungszentrum Dresden-Rossendorf, 01314 Dresden, Germany
$^2$ Max-Planck-Institute for the Physics of Complex Systems, Nöthnitzer Street 38, 01187 Dresden, Germany
$^3$ ICCMP, University of Brasilia, 70904-970, Brasilia, Brazil
$^4$ Institute of Physical Chemistry and Electrochemistry, TU Dresden, 01062 Dresden, Germany
$^5$ Institute of Applied Photophysics, TU Dresden, 01062 Dresden, Germany

E-mail: k.morawetz@fzd.de

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Abstract. A row of parallel ordered and coupled molecular nanoshafts is shown to develop a shuttling transport of charges at finite temperature. The appearance of a current without applying an external bias voltage is reported as well as a natural diode effect allowing unidirectional charge transport along one field direction while blocking the opposite direction. The zero-bias voltage current appears above a threshold of initial thermal and/or dislocation energy.

Organic field effect transistors (OFETs) based on different polymers [1]–[3] attract an increased interest due to numerous potential applications as flexible and low cost storage and microelectronic devices. For achieving excellent electric properties such as high charge carrier mobilities and low resistive losses, which are required for technologically attractive device applications, a high structural ordering of the semiconductor molecular material is necessary [4, 5]. Oligothiophenes and their derivatives can be regarded as one of the most promising systems for building such self-organized structures across multiple length scales due to the variety of intra- and intermolecular interactions, which originates from the polarizability of the sulfur electrons and the aromatic $\pi$-electron system [6]–[8]. Just recently an OFET structure has been built from ultra-thin self-assembly films made from oligothiophenes, which are arranged in a high-order lamellar stacking perpendicular to the substrate surface [3].
In general, the charge transport is largest in the direction perpendicular to the plane of the thiophene rings \([9, 10]\). This finding addresses already the basic difference between electronic transport in organic conductors and in classical semiconductors. Though the band gap between the lowest unoccupied and the highest occupied level of about 3 eV in quarterthiophene suggests an analogy to the conduction and valence band in semiconductors, there are crucial differences. While in conventional semiconductors the transport is due to delocalized states and limited by the scattering, the transport in molecules is due to localized states dominated by hopping \([11]\).

In this paper, we suggest a new mechanism of charge transport which is possible for flexible molecular tubes, shafts or any elastically deformable assembly which could provide an alternative explanation of transport properties in nanoshift-based OFETs. This could be understood as a transport channel which exists additionally besides the hopping. The performance of OFETs based on oligothiophene \([3]\) shows characteristic features, e.g. the current starts at a certain threshold of gate voltage and reaches a saturation value for certain drain voltages. We will show in the following that for a regular arrangement of long elastic molecules a shuttling transport can be established, which can model these features. In particular, we will describe a shuttling effect of nanoshifts leading to a diode behavior as well as to a directed current without external bias voltage. This resembles the ratchet effect described as Brownian motors \([12]–[14]\) also realizable with oscillating laser fields \([15, 16]\). The thermal noise plays an important role for activating such motors to overcome a certain barrier \([17]\). In the effect presented here, the activating threshold is given by an initial kinetic or potential energy necessary for the first nanoshift to reach the contacts.

Shuttling in single-dot devices has already been the focus of some interest \([18, 19]\). Besides promising applications for nanoelectromechanical devices, the coupling of quantized transport with micromechanical cantilevers \([20]\) bridges classical mechanical and quantum physics in an exciting way. Our model, analytically solvable, demonstrates that a similar shuttling mode as known from single-dot transport by mechanical cantilevers is achievable by a row of elastically coupled molecular tubes. The model is based on the coupled spring chain. Despite their simplicity, such models have a surprising ability to describe unknown phenomena of classical quantization phenomena in velocities \([21]\). The model of freely rotating linear chains has been investigated also in view of quantization \([22]\) and has been applied to entanglement problems \([23]\). We note that the shuttling transport described here should not be mixed up with the so-called ‘chain shuttling’ in polymerization reactions, where a growing polymer chain is transferred between different metal catalysts \([24, 25]\).

The elasticity of polymers with respect to the bending and rigidity has been studied by molecular dynamics simulations \([26]\). The model of hard-sphere chains is used to describe the stiffness and diffusion in polymers \([27]\). These elastic properties play an important role in the mesoscale modeling of carbon nanotubes \([28]\). Such carbon nanotubes on glassy carbon electrodes can enhance the current response by a factor of 1000 as reported in \([29]\). Therefore it is of high actual interest to reinvestigate the transport in nanotubes. We will concentrate in this paper on charge transport perpendicular to the direction of nanoshifts.

Specifically, we consider \(N\) nanoshifts of length \(L\) parallel oriented in the \(y\)-direction. The shafts are standing perpendicular on the substrate, and are periodically arranged along the \(x\)-direction at a certain distance from each other (see figure 1). We expect them to couple elastically by their top ends. Then the shafts bend in the \(x\)-direction when applying the tangential
force $F$ with the displacement expansion \[30, 31\]

$$x(z) = \frac{F z^2}{2EI} \left( L - \frac{z}{3} \right) = \frac{3}{2} x(L) \left( \frac{z}{L} \right)^2 \left( 1 - \frac{z}{3L} \right),$$

(1)

where $\mathcal{E}$ is the Young modulus and $I = \int z^2 \, dA$ is the area moment of inertia being $I = \pi r_0^4 / 4$ for circular cross sections of tubes with radius $r_0$ or $I = ab^3 / 12$ for nanoshfts with rectangular cross section of sides $a$ and $b$. The maximal displacement on the top ends at $z = L$ is $x = x(l) = FL^3 / 3\mathcal{EI}$ from which the spring constant $k = F / x = 3\mathcal{EI} / L^3$ is given provided we know the Young modulus. In other words, we have a coupled linear chain of top ends obeying the differential equations $\frac{d^2 x_i}{dt^2} = \omega^2 (x_{i-1} - 2x_i + x_{i+1})$ with $\omega^2 = k m^{-1}$ given by the mass of the nanoshfts. The nanoshfts are located in-between two solid contacts such that the coupled equations are bounded which can be formally expressed by $x_0 = x_{N+1} = 0$. Additionally, each nanoshft can carry a charge $q_i$ which can be exposed to a time-dependent external field $E(t)$. The total coupled equation system for the time dependence of the nanoshft top ends is the same as the one for a coupled spring chain \[32\] and reads

$$\frac{d^2 x_i(t)}{dt^2} = \omega^2 [x_{i-1}(t) - 2x_i(t) + x_{i+1}(t)] + a_i(t)$$

(2)

with the force per mass $\omega^2 = 3\mathcal{EI} / m L^3$ and the acceleration due to the external bias $a_i(t) = q_i E(t) / m$. For simplicity, we will use time in units of $1 / \omega$ below. For quarterthiophene, we have a typical value of $k = 1 \text{ N m}^{-1}$ and a mass of $m = 5.49 \times 10^{-22} \text{ g}$ which leads to the scale $\omega = 1.35 \text{ ps}^{-1}$. The length will be in units of $l_0 = 0.1 \text{ nm}$ as a typical value. The field is given in units of $m \omega^2 l_0 / q = 6.2 \times 10^8 \text{ V m}^{-1}$ again given explicitly for quarterthiophene and the charge current in units of $q \omega = 21.6 \text{ mA}$, where we assume one single charge $q = e$. The typical energy units are $m \omega^2 l_0^2 / 2 = 31.2 \text{ meV} = 362 \text{ K}$.

The analytical solution of (2) obtained by the standard eigenvalue method is given in terms of the normalized orthogonal system $\phi_{n \nu} = \sqrt{2 / (N + 1)} \sin \left[ n \nu \pi / (N+1) \right]$, \[32\]

$$x_i(t) = \sum_{n=1}^{N} \phi_{ni} \left[ (c_n \cos \omega_n t + d_n \sin \omega_n t) + \int_{0}^{t} dt' \frac{\sin \omega_n (t-t')}{\omega_n} \sum_{m=1}^{N} a_m (t') \phi_{nm} \right]$$

(3)

with the eigenfrequencies $\omega_n^2 = 2 (1 - \cos [n \pi / (N+1)])$ \[32\] and the initial condition determining $c_n = \sum_{\nu} \phi_{n \nu} x_{\nu}(0)$ and $d_n = \sum_{\nu} \phi_{n \nu} x_{\nu}(0) / \omega_n$.

Now we proceed by considering the nanoshfts between two oppositely charged plates, $q_{\text{sides}}$, modeling the contacts. Each nanoshft can carry a negative charge $q_i < 0$ describing the charge in the lowest unoccupied molecular orbital or a positive charge $q_i > 0$ for the transport of holes in the highest occupied molecular orbital or none. Each time when two top ends of the nanoshfts touch each other the charge is moved if one of the two tubes had no charge. In the case of opposite charges they annihilate and it is counted as recombination which gives rise to light emission. We consider the thiophene molecules to touch if they are closer than their thickness of $0.4 \Delta x = 1.4 \text{ Å}$. We do not consider a bouncing back of the shafts since the thiophene are soft molecules and far away from a hard sphere behavior. If one nanoshft is touching the contact on one side it contributes to the current on this side as $q_{\text{sides}} - q_i$. Each time such an event happens the time evolution according to the analytical solution (3) restarts with the new initial conditions and new charge distribution. In this way, we use the speed of analytical solution together with the nonlinear process of recharging.
Figure 1. Four snapshots of time evolution (from above to below) of the chain of shuttling nanoshafts (1st column) with positive charge (green) and negative charge (red) or no charge state (grey). The kinetic energy $E$ (2nd column), left (green) and right (red) side currents $J_{\text{right/left}}$ (3rd column) and the number of recombinations $N_{\text{recom}}$ (4th column) is given versus time elapsed.

For exploratory reasons, we restrict ourselves to 11 nanoshafts of length $20 l_0$ and have arranged them at a distance of $3 l_0$. These are typical parameters of quarterthiophene used in recent experiments [3]. First, we charge all shafts equivalently and start the process of shuttling by bending the leftmost tube to the left contact, allowing transfer of the first charge to the left lead.

In figure 1, we have plotted different snapshots of the time evolution in units of $1/\omega$. We see that the system starts to shuttle and to transport positive charges from left to right and negative charges from the right to the left side. This leads to steps in the current counted as charges delivered on the corresponding side per elapsed time. The number of recombinations is increasing with time; complete movies can be found in [33].

The snapshots in figure 1 are actually taken from a run without applying any external field. The gates serve here merely as a reservoir of charges, not as capacitor plates. The astonishing observation is now that even for such an unbiased case a finite total current is developing. This fact is demonstrated in figure 2, where the time evolution of the number of recombinations, the kinetic energy, and the total current which is the sum of right and left currents, are plotted for different external fields. The total current and the recombination rate, $N_{\text{recom}}/t$ reach saturation with increasing time, whereas the kinetic energy remains constant on average. If one applies an
electric field of \( E = 0.2 \) oppositely to the direction of zero bias voltage current, we see that the kinetic energy is decreasing with time and the shuttling current as well as the recombination rate are reduced. In fact, it reaches a state where the left and right half of the tubes shuttle symmetrically against each other such that no net current is delivered. If the field is applied in the opposite direction \( E = -0.2 \), the system is accelerated and delivers more and more charges, limited finally only by the length of the tubes. In other words, we observe a pure diode effect just due to shuttling of coupled chains of nanoshfts. The total current reached after long times for different applied fields is depicted in figure 3 and illustrates this diode effect as a quite systematic one.

One may argue that this diode effect as well as the observation of a current without external bias is due to the initial charging of the nanoshfts. In figure 3, we have plotted the finally reached total current versus the applied field for two cases, the initially charged case considered so far, and the case where initially all shifts are uncharged. We see that identical final currents are obtained without external bias for both cases and the diode effect is present, as well.

Now, we want to return to the puzzling observation that a charge transport occurs even without external bias. To understand the conditions under which such an effect occurs we have to clarify the dependencies on the initial kinetic and potential energy and the geometric configurations. The length \( L \) of the nanoshfts determines only the timescale \( \omega \) and scales out here. Therefore the distance between the nanoshfts \( \Delta x \) in the row is the only geometric parameter left. Further, we determine the initial kinetic and potential energy by the elongation \( x_0 \) and speed \( v_0 \) of the leftmost nanoshft, whereas all other nanoshfts are initially at rest. In figure 4, we plot the dependence of the current reached on the initial displacement and the initial velocity. Using dimensionless units for the velocity \( v^* = v/\omega l_0 \) and the displacement...
\[ J_{\text{tot}} (q/\omega) \]

\[ J_{\text{tot}} (q/\omega) \]

**Figure 3.** The total current versus applied electric field for two cases, initially uncharged tubes and initially charged tubes.

**Figure 4.** The total current without voltage bias versus initial displacement (left) and versus initial velocity (right) of the leftmost nanoshaft.

\[ x^* = x_0/l_0 \]

\[ E_{\text{tot}} = m\omega^2 l_0^2 [(v_0^*)^2 + (x_0^*)^2]/2 \]

where the length unit is \( l_0 \). We see in the right plot of figure 4 that the current increases quadratically with the initial velocity, i.e. the current is proportional to the initially deposited kinetic energy. This initial kinetic energy can be equivalently realized by thermal motion and characterized by a temperature.
In the simulation described so far we bend the leftmost nanoshift sufficiently close to the electrode such that the shuttling can happen even without initial kinetic energy. If we bend it less we obtain a threshold in kinetic energy analogously to the thermal threshold in Brownian motors [17]. The dependence of the current on the initial position is seen in the left plot of figure 4. We have chosen an initial velocity below the threshold which shows that a threshold in the position or potential energy has to be overcome in order to create the shuttling current. We note that the shuttling transport develops only if we start with asymmetric initial conditions. Otherwise counter-oscillations of the left and right half of shafts block any transport. Therefore the symmetry breaking is due to initial conditions and this model illustrates an electronic ratchet effect with thresholds in kinetic or potential energy corresponding to a high system temperature or initial elongation being \( m\omega^2\Delta x^2/2 = 281 \text{ meV} \) for the example of quarterthiophene used here.

As already discussed above the threshold in the initial velocity of one shaft represents the required initial kinetic energy to allow a charge to flow. A thermal excitation would therefore enhance this flow and would lead to a higher current.

Note also that in this picture we have neglected the effect of Coulomb interaction between the charges in the shafts and have taken only the Coulomb effect of the charges with the external bias into account. This picture is based on the very small density of electrons per thiophene molecule (\( \sim 10^{-6} \)). Indeed a crude estimate of the Coulomb energy between two adjacent charged shafts, \( e^2/4\pi\varepsilon_0\Delta x \), divided by the number of shafts as approximation for the density leads to \( E_{\text{Coul}} \approx 0.48 \text{ eV} \) for our situation of \( \Delta x = 3.5 \text{ Å} \). This is an upper estimate, since we do not have all shafts charged simultaneously. If we compare this with the total initial energy \( E_{\text{tot}} = m\omega^2 l_0^2 [(v_0^*)^2 + (x_0^*)^2] / 2 = 0.031 \text{ eV} [(v_0^*)^2 + (x_0^*)^2] \) due to elongation, we see that the Coulomb energy is equivalent to an initial velocity of one shaft of maximal \( v_0^* \approx 2.8 \). This means the Coulomb effect between the charges of the shafts is of the same order as the energy due to elastic deformation assumed as the source of the shuttling. In other words the mechanism proposed here should be taken into account besides Coulomb effects when considering the transport between elastic molecules like thiophene. The Coulomb effect on the hopping transport has been discussed, e.g. in [34]. One might expect that the Coulomb effect will lead to a blocking of the transport due to the creation of a Coulomb gap. This has to be further investigated.

In summary, we have found that a chain of perpendicularly arranged coupled and chargeable nanoshifts shows a shuttling transport of charges. As a surprising effect it turns out that a finite current is established already without external bias only due to the initial asymmetric deformation of the nanoshifts. The effect observed here is reminiscent of the ratchet effect. Even in the absence of a net macroscopic force or noise, a current can be generated. This resembles to a great extent the prominent motor proteins found inside cells. There, proteins such as myosin and kynesin use chemical energy which is gained from hydrolysis of ATP into ADP to move along asymmetric pathways transporting vesicles inside cells, contracting muscles and being important in the process of cell division [13, 14]. Concerning the transport between thiophene molecules, we believe that besides the hopping, the shuttling transport channel described here is of importance. At least the comparison with the Coulomb effect shows the same order of magnitude. In a forthcoming work, we will discuss the hopping transport for the specific thiophene molecules in detail [35].
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