

What might be there to affect the I-V

Contact effects

We have discussed the issue of contact limited injection and we have defined it according to the density at equilibrium that is created at the semiconductor (polymer) near the contact. A different definition might be related to the dynamics near the contact and it will be defined according to the current a contact (interface) is able to support.

If for simplicity (as an example) we assume the contact injection is via thermionic emission: $J_T = A^* T^2 \exp(-\Delta E / kT)$

and the current in the bulk is space charge limited: $J_{SCL} = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3}$

At a high enough voltage the current in the bulk may become comparable to the current the contact can support and the device current becomes contact limited. This happens at a

critical voltage: $V_c = T \left(\frac{8A^* d^3}{9\mu\epsilon} \right)^{0.5} \exp(-\Delta E / 2kT)$. If we account for contact barrier

lowering due to image force at metallic contacts: $V_c \Rightarrow V_c * \exp(\beta F^{0.5} / 2kT)$.

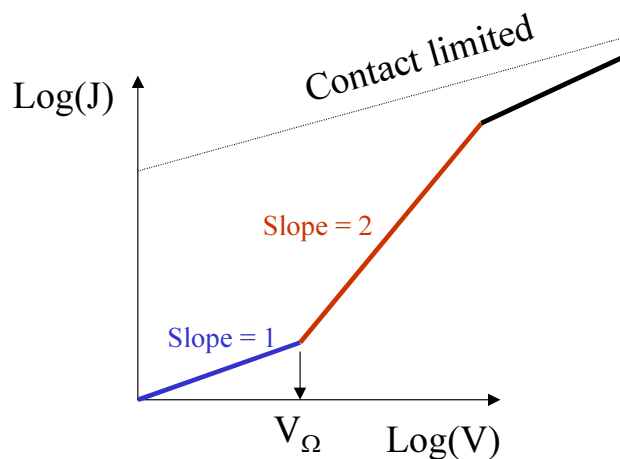


Figure 1. The effect of the contact becoming a limiting factor at high voltages

Single --> Double injection

In the case of single carrier space charge limited current one employs one good contact and one with a relatively high injection barrier. The SCL condition dictates that at the good contact the electric field is zero (approx) and at the other contact it is up to $1.5V/L$. As we increase the applied voltage the effect of barrier lowering at the "bad" contact enhances the injection and the device may turn into a double injection device. Namely, both contacts become good injecting contacts. In this case it could be that the presence of the two charge types screens the SC field and the device is no longer SCL. Or, if the recombination is fast, half of the device is electron SCL and half is hole SCL. The characteristic I-V is functionally similar with the single carrier mobility being replaced by an effective mobility.

Field dependent mobility

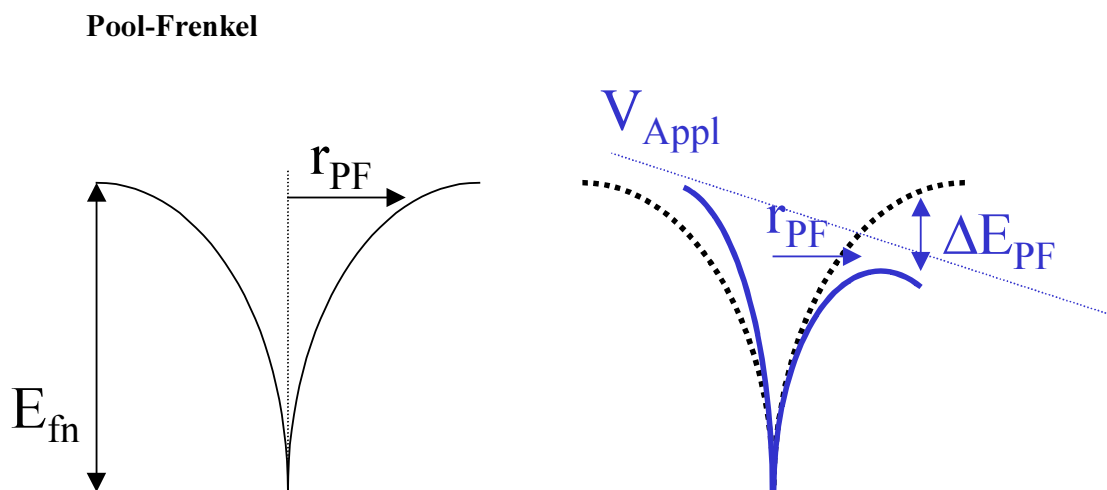


Figure 2. Schematic description of a potential trap created by a static charge (left) and the lowering of the trap under applied voltage (right).

In the Pool-Frenkel picture we assume the existence of a trap made of a static positive (negative) charge. When a negative (positive) charge is captured the trap becomes neutral (and full). We can define the trapping radius as the distance at which the

trap potential equals kT . When a bias is applied the trap potential varies in a manner similar to the Schotcky effect. In a 1D picture one can write the potential as:

$$\phi = -\frac{q}{4\pi\epsilon} \frac{1}{r} - F \cdot r \text{ where } F \text{ is the applied electric field.}$$

$$\text{To evaluate the lowering: } \frac{d\phi}{dr} = 0 \Rightarrow \begin{cases} r_{PF} = \sqrt{\frac{q}{4\pi\epsilon F}} \\ \Delta E_{PF} = \sqrt{\frac{q}{\pi\epsilon}} F^{0.5} \end{cases}$$

The current under such conditions behave similar to the thermionic emission current in the Schotcky formalism:

$$I_{PF} \propto F \exp\left(\frac{-q\left(\Delta E - \sqrt{\frac{qF}{\pi\epsilon}}\right)}{kT}\right)$$

$$I_{Schotcky} \propto AT^2 \exp\left(\frac{-q\left(\Delta E - \sqrt{\frac{qF}{4\pi\epsilon}}\right)}{kT}\right)$$

We note that as the trap is lowered the current grows super-linearly which can also be described as a field dependent mobility.

There are many models in the literature describing the effect of traps depending on its type or the energy/density distribution of the traps.

Transport in Organics

Since there are many mechanisms having similar I-V signature it is essential to build the relevant physical picture to assist us pick the right mechanism. As we have seen, in the previous lectures, organic polymers are more amorphous than crystalline or as we will see more disordered than ordered. Namely, the concepts of delocalised bands or band transport is not strictly applicable. Lets start with a bit of intuition regarding the mechanisms occurring in a polymer film.

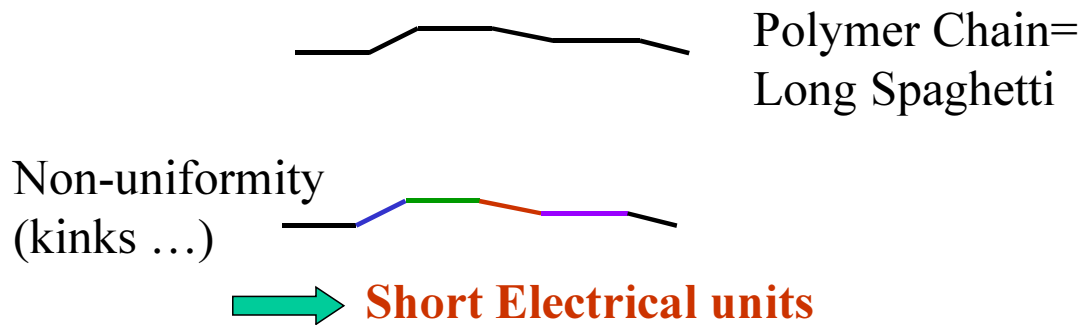


Figure 3. Conceptual description of a polymer made of small electronic units (conjugation lengths).

As we know well by now one doesn't find electronic continuity across the entire polymer chain and due to non-uniformity (physical or chemical) the electronic continuity is limited to a shorter range of typically 10 ± 3 monomer units. The non-uniformity not only breaks the electronic continuity (conjugation) but it also creates different environment (potential, polarisation, dipoles,...) at different positions in the film. Namely, when we go from one conjugation unit to the other we would expect fluctuations in the energy gap (HOMO-LUMO) and the absolute position of the bands. Moreover, if we account of the effect caused by interchain coupling then the fluctuations in the distance between neighbouring chains becomes important too.

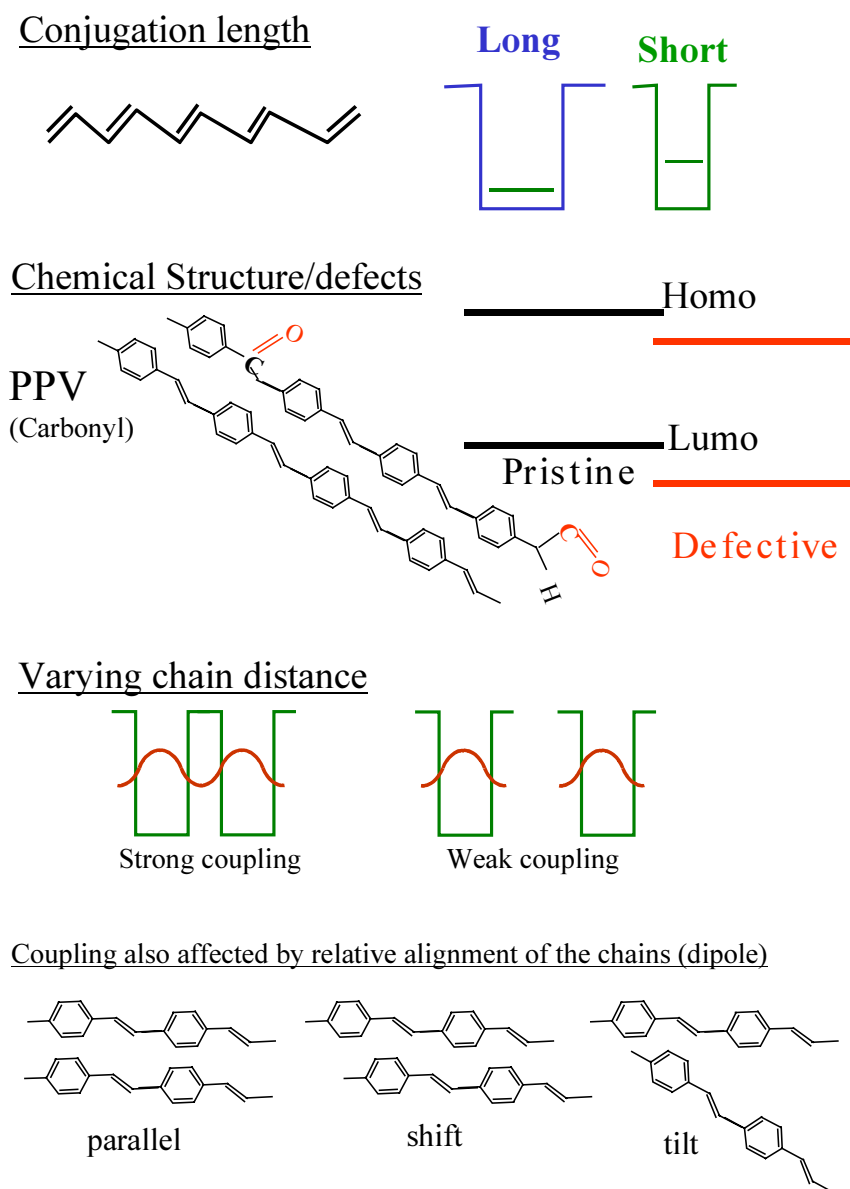


Figure 4. Structural factors affecting the transport.

In some cases we find the situation of polycrystalline or regions of aggregation where the transport is different at different regions. Having all this in mind we can think of a (very simple) model system:

Model System

Collection of Molecules
having varying size and
varying distance

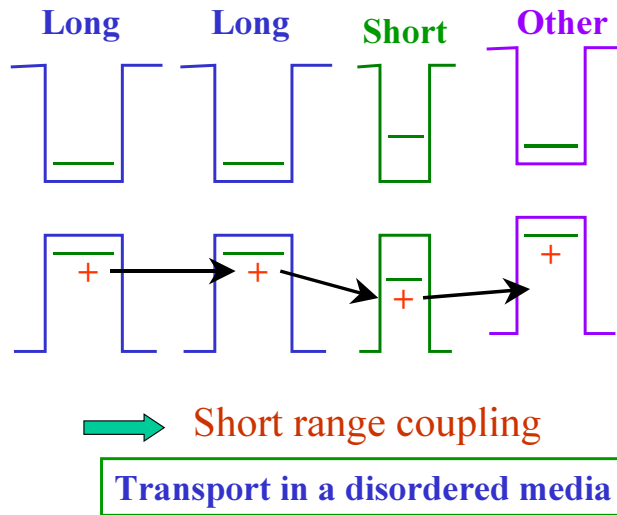


Figure 5. Conceptual description of the transport in organic polymer (molecule) films.

This model for transport (which is phonon assisted tunnelling) is known in the literature as hopping transport. The hopping occurs from localised state j to localised state i with the aid of a phonon. Hence, the transfer rate will depend on the phonon frequency (ν_0), the tunnelling probability, and the probability to absorb a phonon.

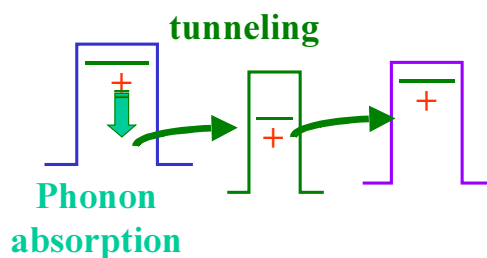


Figure 6. Phonon assisted tunnelling. Note that the phonon is only needed for upward jumps.

Placing the above into formal equations results in:

$$W_{ij} = \underbrace{\nu_0}_{\text{Phonon frequency}} \underbrace{\exp(-2\Gamma R_{ij})}_{\text{Tunneling}} \left\{ \begin{array}{ll} \exp\left(-\frac{\varepsilon_i - \varepsilon_j}{k_B T}\right) & \varepsilon_i > \varepsilon_j \\ 1 & \varepsilon_i < \varepsilon_j \end{array} \right. \underbrace{\text{Boltzman factor (phonon absorption)}}_{\text{Boltzman factor (phonon absorption)}}$$

The tunnelling factor is similar to what we have seen in the Dexter transfer mechanism where Γ is the inverse localisation length and R_{ij} is the distance between the localised states. Note that a factor representing the probability to find a phonon (phonon occupancy factor) is not part of the formalism. We assume that all phonon frequencies are equally available and no preference is given to frequencies associated with the molecular vibrations. This seems to contradict the discretisation of phonon energies (frequencies) that was required to produce the emission spectra but we will ignore it at this stage. The above expression assumes we can separate the problem into two: spatial function (tunnelling) and energetic function (Boltzman factor). The energetic factor simply states that in order to better couple state i with state j one need to "pump" energy into the system. The usual source is thermal which are in fact the phonons or the molecular motions.

The factor that is not accounted for is the polaronic nature of the charge carriers or the "molecular-view" that describes a transition as a motion across the configuration-coordinate space (see Figure 7). In this picture the transition from site i to site j is easiest (overlap integral = maximum) when the two sites look the same (share the same configuration-coordinate). The enhancement of the transfer between i and j is dependent on the molecular motion that will bring the two sites to a similar configuration. In other words - there is a thermal activation even for states of lower energy. The effect of this on the transport has been treated recently by Scher¹.

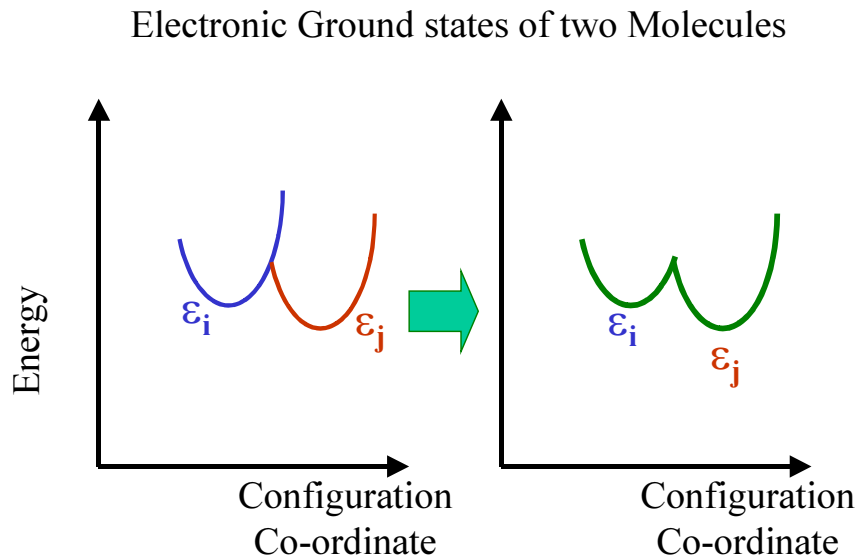


Figure 7. Electronic transition between two states in the configuration-coordinate space. The left shows the two states separated and the right the combined potential. Note the "strange" barrier for going down in energy.

As in any system with random variables the statistics used to describe the variations is of key importance. If we are interested in transport across a large distance then we can use the universal Gaussian distribution. I am not sure what a "large distance" is in the current context and will add it once I am. It could be that the answer for that is hidden in Monte-Carlo simulations that suggest that it may take microns for the carriers to reach the "equilibrium" state.

Gaussian Distribution of States (rough energy surface)

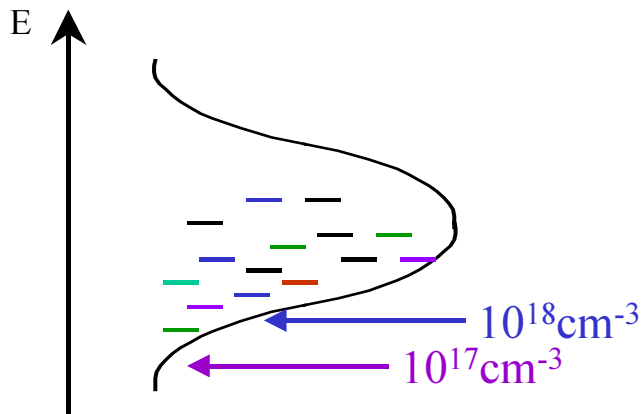


Figure 8. The Gaussian distribution of energy states.

So what will happen to the carriers once they move across an energy surface which has a distribution of distance and energy levels? Imagine a row of cars driving across a field with random distribution of holes or sandpits (Figure 9).

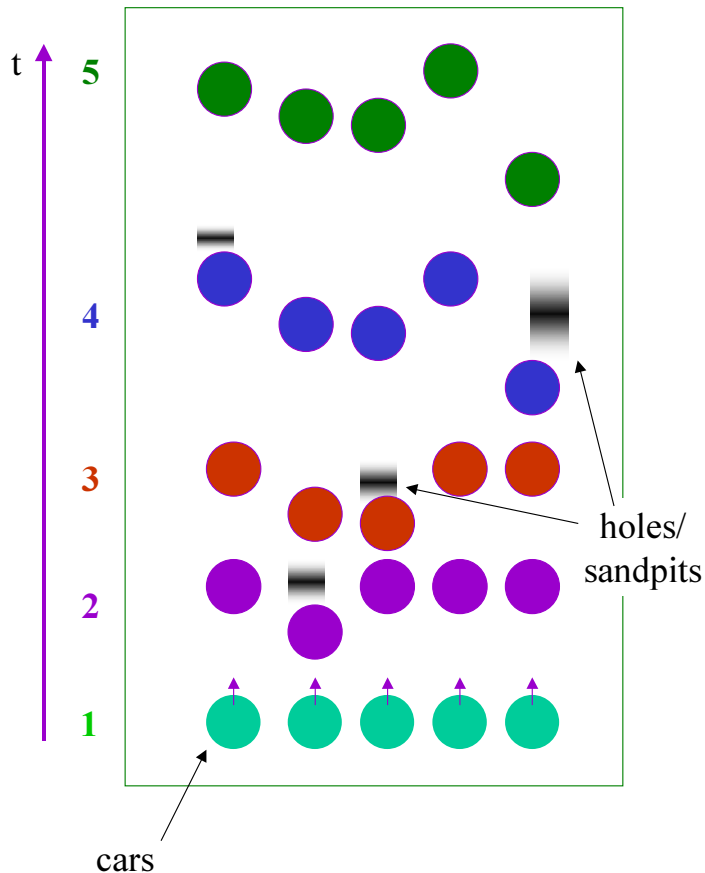


Figure 9. The effect of holes (sandpits) on cars rolling down a field.

At first all the cars move together in a straight line ($t=1$) at the "injection" position. At this stage the velocity (mobility) of the cars is well defined. Once a car crosses a "hole" it slows down and is being delayed by (or in) the sandpit. As more cars cross holes of different depths (lengths) the cars distribution broadens. Note, there is nothing equivalent to the classic diffusion in our model and hence the velocity (mobility) and the broadening (effective diffusion) are not necessarily related according to Einstein's relation. Looking at Figure 9 a question arises- **how do we define the cars velocity (mobility)? How do we measure it?**

Fastest car: If we define it as the length of the field divided by the time it takes the first car to cross it we actually say that the front of the car packet defines the mobility. In this case for a field half as long we would find a higher mobility since the probability to find a car that hasn't crossed a hole (fast car) is an inverse function of the distance. So we expect to find a mobility that is decreasing as a function of device length. We can also

expect that for fields longer than a certain value the mobility will become less length dependent. The length at which this will happen depends strongly on the "holes" (waiting time) statistics and in some scenarios may be considered as "infinite".

Average velocity: Using the average position of the cars seems to be a more reliable way of defining the velocity. However, there is more than one way to average numbers. If we assume that the cars have traversed along enough distance to acquire the shape of a Gaussian then the average velocity would be defined as the arrival of the centre of the Gauss. Again, there is a certain distance required for the Gauss to reach a constant velocity (if ever). However, one would expect this method to be more robust compared to the "fastest car" method.

In an "extreme" case it might be almost impossible to define a mobility. If the spreading of the "cars" is such that they completely fill the "field" then some cars actually do not move at all and the definition of mobility becomes questionable. This will be found in transport under local non-equilibrium conditions (energetic and between sites) and such a sample would show pronounced memory effect (non-Markoffian transport).

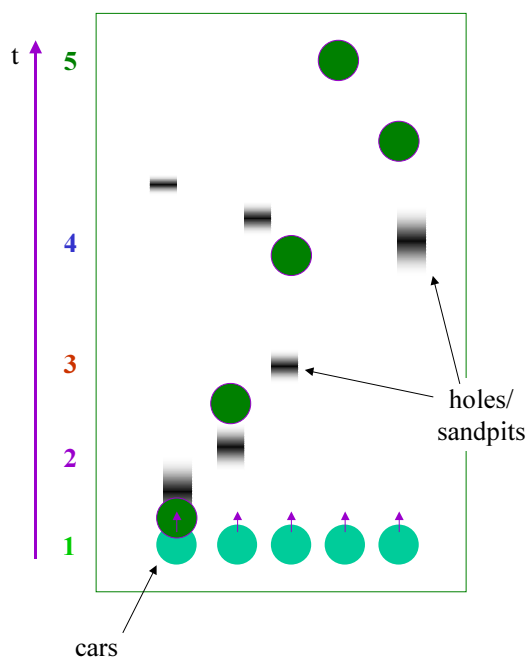


Figure 10. The extreme case of "cars" spreading across the entire sample.

Dispersive transport

If the charges, as they cross the sample, never reach a constant velocity (i.e. "mobility" keeps going down) then the transport is termed dispersive. There is dispersion in the transport times and one can not truly define or deduce an "intrinsic" mobility. The occurrence of dispersive transport depends on the material (and chemical purity), sample thickness, temperature, and probably also the applied electric field. A quote from a paper by Scher and Montroll (PRB, 12, 2455, 1975) "*If one insists on the conventional relation $\mu = L^2 / t_T V$ to define an effective μ , then, besides the possibility of an apparent field dependence, one would have to rationalize a thickness dependence of μ* ". This quote tells us two things: first, "*unless the mean $\langle l \rangle \propto t$ the idea of a $\mu = L^2 / t_T V$ depending on the material only may break down*" and second, The way μ is defined (measured) is critical.

In the context of polymer LEDs we can see in the paper by Pinner et. al. (JAP, 86, 5116, 1999) that an effort was made to find a criteria for μ whilst choosing experimental conditions that minimise memory effects.

Waiting time distribution (WTD)

The above picture was driven by the occurrence of disorder in the energy and position of the transport sites. Within this picture one can describe the transport by defining the time a carrier spend at each site before moving to the next. For a classical Gaussian transport the WTD is $\psi(t) \propto e^{-\lambda t}$ where λ is a single transition rate. A case of very high dispersion can be found in $\psi(t) \propto t^{-(1+\alpha)}$ which will show non-Markoffian behaviour as in Figure 10. As Figure 11 shows the above non-Markoffian case resembles the effects introduced by deep trapping. Many times the actual mechanism lies between the classical Gaussian and the non-Markoffian picture and is described using the Wij term in Monte-Carlo simulations.

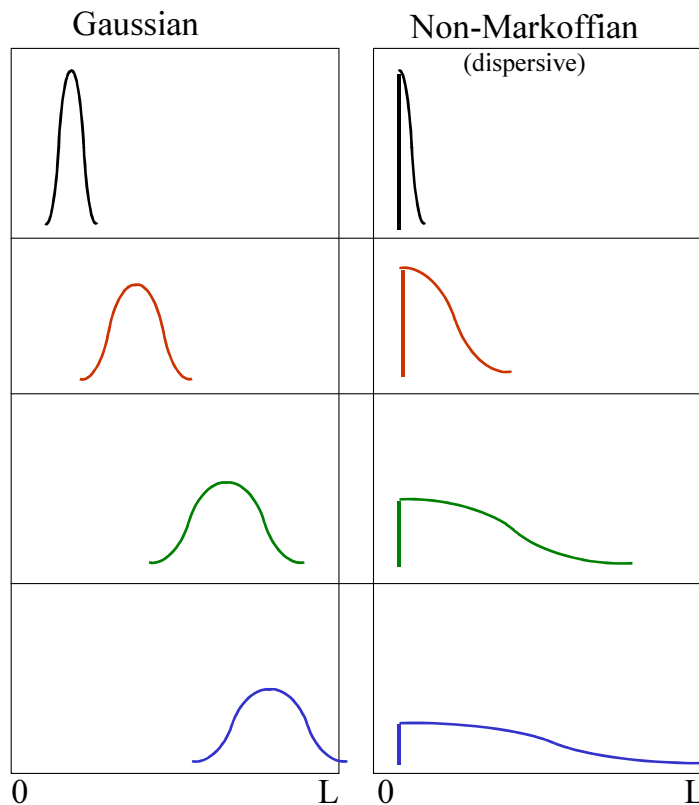


Figure 11. Carrier packet spreading through a sample under applied electric field. The Gaussian case is on the left and the highly dispersive and non-Markoffian is on the right.

Time of flight measurements

Before considering the effects associated with the above theories/picture let us consider the experimental framework for which they were developed- the time of flight (TOF) technique.

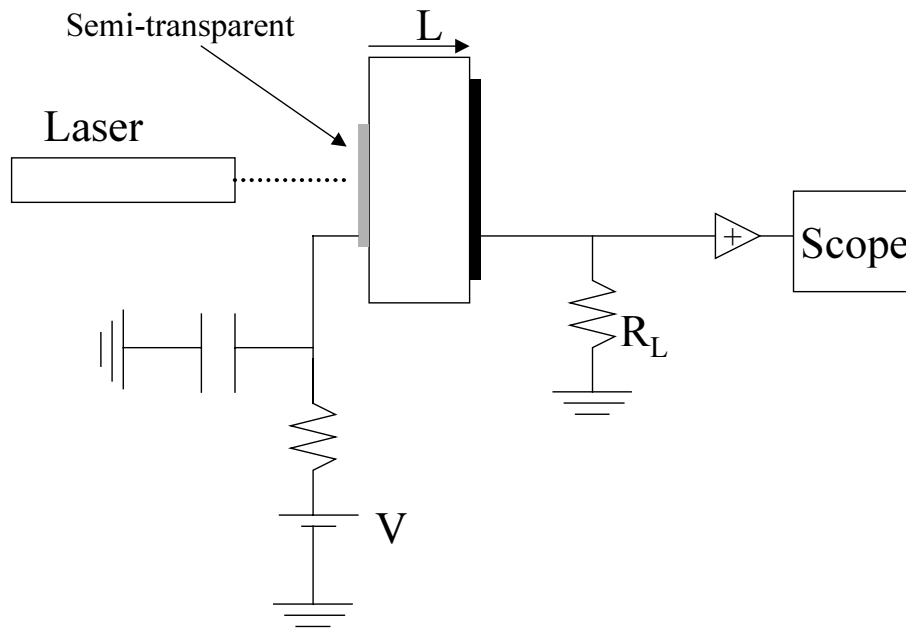


Figure 12. TOF experimental setup (after, M.V. der Auwerar et.al., adv mat, 6, 199, 1994).

**** Add at a later stage- TOF curves, diffusion broadening, W parameter, effective D due to disorder, expressions for mobility *****

Comment - what I write below shouldn't be considered as *the truth* (criticism is welcome).

The above discussion may leave the impression that there might be a confusion regarding the term mobility in the literature dealing with transport in organic polymers. If we want to design devices it would be very convenient if one could use the concept of mobility and its implication. Can we really do that? The discussion above shows that we should approach this concept very carefully. We need to consider what it actually means in a disordered sample and how we can extract it. Just to illustrate the complexity we refer the reader to the high quality experiments reported by Blom et. al. In the initial papers² the mobility is evaluated using CW I-V curves and by showing that at low voltage the characteristics are as the classic space charge limited current (function of voltage and device length) a mobility value is extracted. On the other hand, using a time resolved technique³ the same author using the same material finds that the concept of mobility is ill defined in these materials due to mechanisms described in the Scher-Montroll theory (Scher and Montroll, PRB, 12, 2455, 1975). There shouldn't be any doubt that each of these reports stands on firm ground and that by applying the various theories further insight into the inner physics can be gained. However, without going into the physics of polymers, it feels that something is not right. For CW measurement there is a mobility value and for transient measurements there isn't? Who is right? Is the term "right" appropriate in this context?

These are important questions on the border of physics and philosophy however one would still like to "communicate" between not only research groups but also device structures via a well-defined concept. Since the CW I-V curves are of a global nature it makes sense to define these as the "*correct*" way of extracting mobility to be used in LED device configurations. This is nice but what can one do if the device at hand is not SCL and the I-V curve is not so straightforward to analyse? In such case there is practically no choice but to use a transient method. Can we make it "reliable"? Probably not in the full sense of it but maybe we can design it so that it would correspond to the mobility that would have been extracted if the device was truly single carrier SCL device. This approach is more on the border of physics and engineering than on the border of physics and philosophy.

To implement this physics-engineering approach a numerical device model was devised and compared to experimental results⁴. As a first step it was verified that the universal features of the experiments are reproduced by the model. Once this was established the model was used to determine a method for the extraction of mobility (hopefully) based on the universal features. Using the model we found that if the mobility

is to be calculated as $\mu = \frac{L}{\Delta t E_{appl}}$ then Δt is to be taken as the point where the slope of

the rise changes (on log scale). The way this was found was using the numerical model and knowing the mobility used by the model we can easily calculate $\Delta t = \frac{L}{\mu E_{appl}}$. Next

we looked at the light turn on traces hoping to find a clear signature at the time corresponding to Δt . Fortunately there was such an indication and it was the change of slope in the rise of the EL. Using the numerical model we looked at the charge distribution as a function of time and found that the change of slope corresponds to the time where the hole distribution reaches steady state. This tells us that there is also a physical meaning to this point and that it is most likely to agree with CW I-V which are steady state measurements. It is obvious that in the model there will be an agreement since we found Δt by using the same μ as used in the CW I-V expressions. The real test was done using experimental transient curves as well as CW-IV curves. Indeed it was found that for SCL devices the new method for extracting μ from transient EL is in good agreement with the CW-IV curves --> Mission accomplished.

Since the good agreement was found for a very short device (~80nm) we were convinced that the new definition is more robust than the one based on the turn on point (which favours the fastest carriers).

As we said, using transient method where CW-IV SCL can be applied is not of practical importance, in the current context, so next we extracted mobility from contact limited devices based on the PFO polymer. In this case not only we were able to extract both hole and electron mobility in a single device but we also found that the hole mobility was in good agreement with measurements made by the Sheffield group on microns thick devices using the TOF technique⁵. These results show that the method is rather powerful. We note that in⁴ there is also a list of precautions one needs to take to produce a clean

result one of which is a way of avoiding interference introduced by memory effects (see ⁴).

The last point that finally convinced us that all the above was not just pure coincidence is described in ⁶. Again, using a simple theory we devised a method of time resolving the space charge induced internal electric field. We found (both experimentally and numerically) that the SCL induced field reached a maximum at the point where the slope of the rise in the EL changes. Namely, our method of defining μ is based on the point in time where the device reaches the highest charging point. The maximum charging point is also used in methods based on transient SCL current (not EL) ⁷ and hence this verifies the self-consistency of our new method.

References

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