

Charge carriers in amorphous organic semiconductors: transport, injection and recombination in the correlated energy landscape

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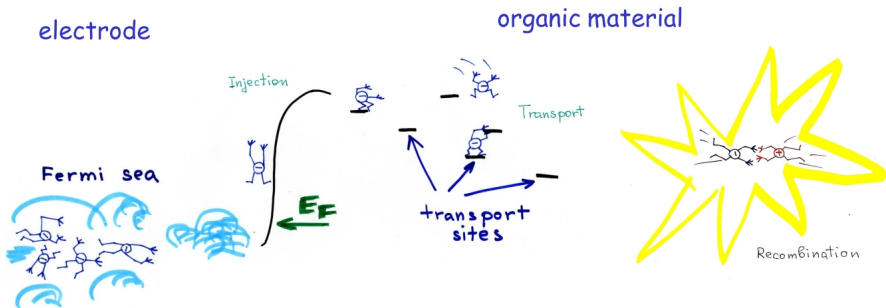
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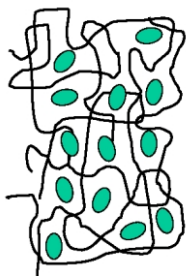
October 19th, 2023

- Major processes in organic amorphous semiconductors: charge carriers' injection, transport, and recombination.
- Density of states.
- Why correlations?
- Charge transport.
- Ingection.
- Recombination.
- Conclusion.

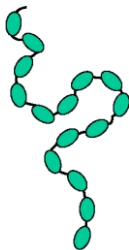
Major processes in organic amorphous semiconductors



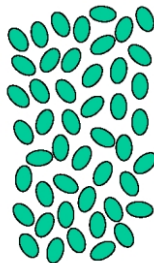
Typical classes of amorphous organic materials used in organic electronics



Molecularly Doped Polymers (MDP)



Polymers with transport sites in the main chain



Small organic molecules

All such materials are disordered materials. Typically, no long range order has been found. Disorder dictates major characteristics of charge transport, injection, and recombination.

Hopping transport

Electronic bands in organic crystals are very narrow (30-50 meV). Disorder leads to the localization. Hence, charge carrier transport in amorphous organic materials is a hopping transport: carrier movement occurs as a series of hops between localized states (transport sites). Hopping transport occurs because of small overlap of the wave functions of transport sites, and the hopping rate exponentially decays with distance (r_0 is the localization radius)

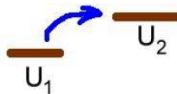


$$\Gamma \propto \exp(-2r/r_0)$$

Hopping rate depends on the difference $\Delta U = U_2 - U_1$ between energies of the final and initial sites: $\Gamma = \Gamma(\Delta U)$.

Miller-Abraham hopping rate:

$$\Gamma = \Gamma_0 \begin{cases} \exp(-\Delta U/kT), & \Delta U > 0 \\ 1, & \Delta U < 0. \end{cases}$$



Mobility dependence on concentration of transport sites

If hopping rate depends on distance as

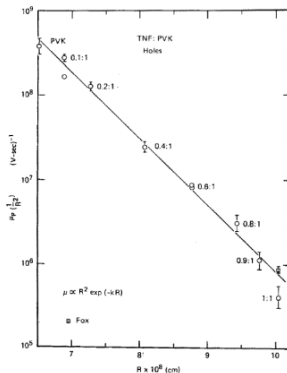
$$\Gamma_{i \rightarrow j} \propto \exp(-2r_{ij}/r_0)$$

then we should expect in the leading approximation

$$\ln \mu \propto -R/r_0$$

where R is the average distance between nearest neighbors.

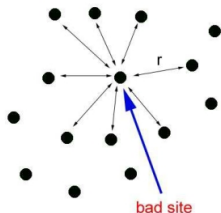
Experiment:



W.D. Gill, J. Appl. Phys. 43, 5033 (1972)

Positional and energetic disorder

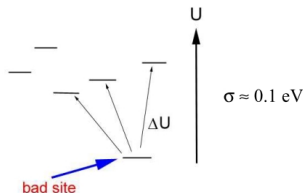
Sites with $\Gamma_{esc} \ll \Gamma_0$ are very important, $\langle \tau \rangle \propto 1/\Gamma_{esc}$.



$$\Gamma \propto \exp(-2r/r_0)$$

Small in both directions

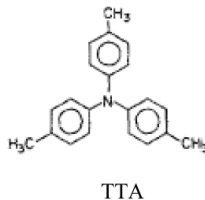
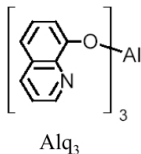
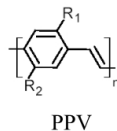
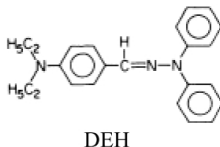
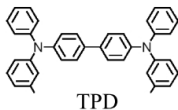
Energetic disorder is more effective for trapping carriers. In the first approximation we can neglect the positional disorder and consider a lattice model with energetic disorder only.



$$\Gamma_{\uparrow} \propto \exp(-\Delta U/kT)$$

$$\Gamma_{\downarrow} \propto 1$$

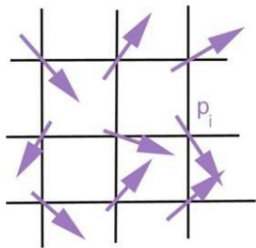
Common organic transport materials



Common feature - all molecules have permanent dipole or quadrupole moments.

What is the source of energetic disorder: dipole glass model

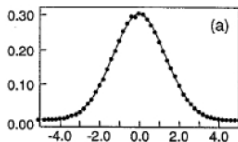
Experimental data shows that increase in the polarity of material leads to low mobility (polar transport material, polar polymer binder, polar inert additives). The simplest reason is that dipoles give a contribution to the total disorder.



$$U(\mathbf{r}) = e \sum_i \frac{\mathbf{p}_i \cdot (\mathbf{r} - \mathbf{r}_i)}{\epsilon |\mathbf{r} - \mathbf{r}_i|^3}$$

$$g(U) = \frac{N_0}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{U^2}{2\sigma^2}\right)$$

$$\sigma = 2.35 \frac{ep^2}{\epsilon a^2} \approx 0.06 - 0.1 \text{ eV}$$

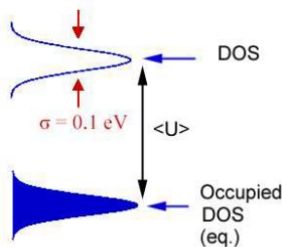


Simulation: Dieckmann et al.,
J. Chem. Phys. 99, 8136 (1993)

Analytic solution: Novikov and
Vannikov, JETP 79, 482 (1994)

Gaussian DOS is guaranteed by the slow decay of the potential of a dipole $\phi(\mathbf{r}) \propto 1/|\mathbf{r} - \mathbf{r}_n|^2$. In the total sum many terms give the contributions, so the Central Limit Theorem is applied and the resulting distribution has a Gaussian shape.

Transport: $\mu(T)$, Gaussian DOS, simple estimation



$$g(U) = \frac{N_0}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{U^2}{2\sigma^2}\right)$$

$$\langle U \rangle = -\sigma^2 / kT$$

$$g_{eq}(U) = \frac{N_0}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(U - \langle U \rangle)^2}{2\sigma^2}\right) \propto g(U) \exp(-U / kT)$$

$$\ln \mu \propto \frac{\langle U \rangle}{kT} = -\left(\frac{\sigma}{kT}\right)^2$$

Transport: $\mu(T)$, experiment

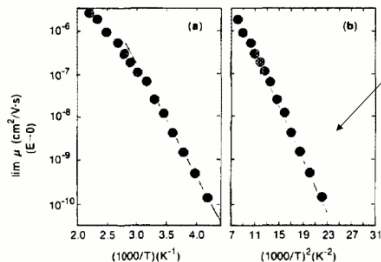


FIG. 10. The intercept in Fig. 8 gives the temperature dependence of f_1 . In (a) we try T^{-1} ; in (b) we try T^{-2} . Clearly, T^{-2} is a better fit.

4291 J. Appl. Phys., Vol. 60, No. 12, 15 December 1986

In the weak field the mobility usually follows the law

$$\ln \mu \propto -1/T^2$$

Simulation gives

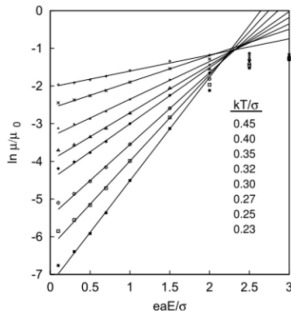
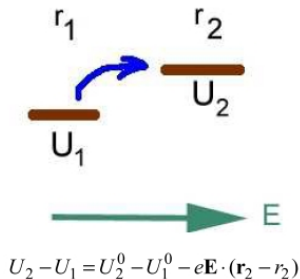
$$\ln \mu \approx -A \left(\frac{\sigma}{kT} \right)^2, \quad A \simeq 1$$

$$\sigma \approx 0.05 - 0.1 \text{ eV}$$

Mobility field dependence: what we should expect

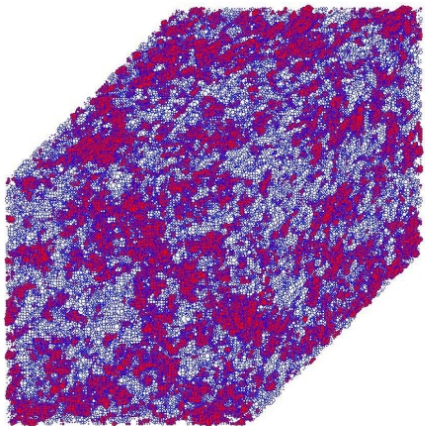
For the quasi-equilibrium transport the limiting stage is the carrier escape from the deep states. If we apply the electric field E then ΔU becomes smaller by $\simeq eER$ (R is the typical distance between sites) so we should expect

$$\ln \mu \propto eER/kT$$

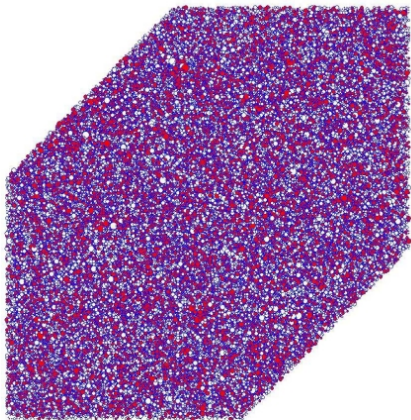


Simulation for the GDM (Gaussian Disorder Model)

Distribution of energies for two models



Dipolar Glass model



Gaussian Disorder Model
(non-correlated distribution)

Simple explanation for the reason for the spatial correlation

Suppose that the carrier energy is the sum of contributions from random sources (for example, dipoles or quadrupoles)

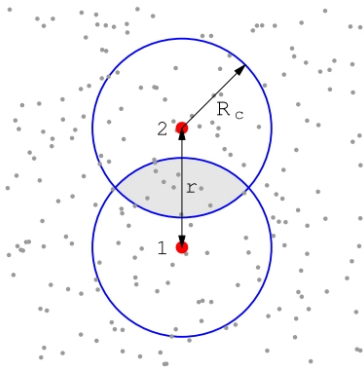
$$U(\mathbf{r}) = \sum_n f(\mathbf{r}, \mathbf{r}_n)$$

where $f(\mathbf{r}, \mathbf{r}_n)$ is a contribution from one source to $U(\mathbf{r})$ and for the sake of simplicity we assume that $f(\mathbf{r}, \mathbf{r}_n) = 0$ for $|\mathbf{r} - \mathbf{r}_n| > R_c$. Then the correlation function

$$C(\mathbf{r}_2 - \mathbf{r}_1) = \langle U(\mathbf{r}_2)U(\mathbf{r}_1) \rangle$$

is nonzero for $|\mathbf{r}_2 - \mathbf{r}_1| < 2R_c$ due to the existence of the region (dark color) where sources give contributions both to $U(\mathbf{r}_2)$ and $U(\mathbf{r}_1)$.

Conclusions: 1) spatial correlation of $U(\mathbf{r})$ does not require correlation of sources; 2) the longer is the range of sources, the slower is the decrease of the correlation function.



For the dipole glass model
 $C(\mathbf{r}) \approx A\sigma^2 \frac{a}{r}$, $A \simeq 1$, a is the lattice scale.

Cluster distribution on size

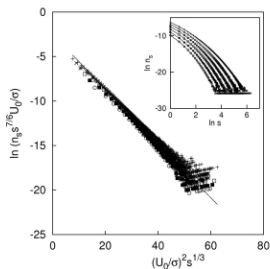
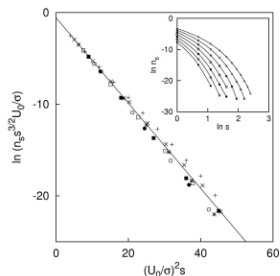
Non-correlated field

$$n(s) \propto \frac{1}{s^{3/2}} \exp\left(-B \frac{U_0^2}{\sigma^2} s\right)$$

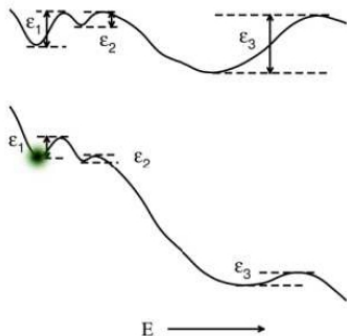
Dipolar glass

$$n(s) \propto \frac{1}{s^{7/6}} \exp\left(-B \frac{U_0^2}{\sigma^2} s^{1/3}\right)$$

Here s is the number of sites in a cluster, U_0 is the boundary energy. Good approximation for $U_0 \gg \sigma$ and $s \gg 1$.



Transport: why correlated disorder is different?

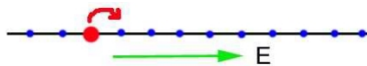


Deep valleys are wide, they are tilted by the field. Important are valleys with the critical size $l(E, T)$ which keep carriers for the longest time. Critical size depends on E and T . Hence, the estimation for the mobility is

$$\ln \mu \propto eEl(E, T)/kT$$

D.H. Dunlap et al, J. Imaging Sci. Tech., 43, 437 (1999).

Transport: 1D model



1D diffusion in random energy landscape $U(x)$

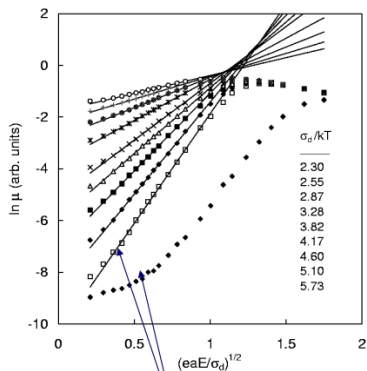
$$\frac{\partial n}{\partial t} = D_0 \frac{\partial}{\partial x} \left[\frac{\partial n}{\partial x} + \beta \left(\frac{\partial U}{\partial x} - eE \right) n \right] \quad \longrightarrow \quad v = \mu E = \frac{D_0}{\int_0^\infty dx e^{-eEx/kT} \left\langle \exp \left(\frac{U(0) - U(x)}{kT} \right) \right\rangle}$$

For the Gaussian DOS and power law correlation function $C(\mathbf{r}) = \langle U(\mathbf{r})U(0) \rangle \propto 1/r^n$
we obtain for strong disorder $\langle U^2 \rangle / (kT)^2 \gg 1$

$$\ln \mu \propto E^{-n/(n+1)}$$

Dunlap et al. *PRL* 77, 542 (1996)

Transport: simulation for dipole glass



Simulation data for the lattice model suggest

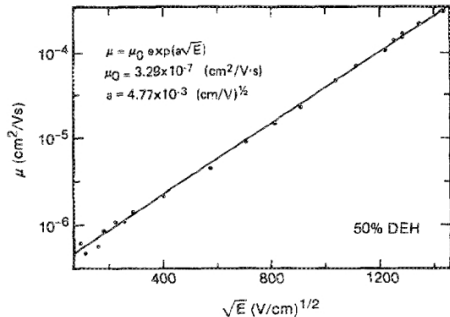
$$\ln \mu / \mu_0 = -\left(\frac{3\sigma}{5kT}\right)^2 + C \left[\left(\frac{\sigma}{kT}\right)^{3/2} - \Gamma \right] \sqrt{eaE/\sigma}$$

here a is a lattice scale, $C = 0.78$, $\Gamma = 2$.

The bottom curve is the result for the uncorrelated disorder (Gaussian disorder model) for $\sigma/kT = 5.1$.

Novikov et al., PRL **81**, 4472 (1998)

Mobility field dependence: experiment



Data for the polycarbonate film doped with organic transport dopant.

Poole-Frenkel field dependence

$$\ln \mu \propto \gamma(T) \sqrt{E}$$

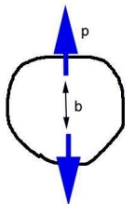
Schein et al., *J. Appl. Phys.* **66**, 688 (1989)

Using the temperature dependence of the slope one can estimate σ_{corr} . Typically, $\sigma_{\text{corr}} \approx \sigma_{\text{total}}$. In organic materials the dominant part of the disorder is a highly correlated disorder.

Nonpolar (quadrupolar) materials

Disordered nonpolar material may be considered as a quadrupolar glass – (dipoles are replaced with quadrupoles). Quadrupolar molecule may have two identical polar groups oriented in the opposite directions.

Then the total dipole moment $\mathbf{P}_{\text{tot}} = 0$,
but the quadrupole moment $Q = pb \neq 0$.



For a lattice model
$$\sigma^2 = \frac{4e^2 Q^2 c}{5\epsilon^2} \sum_n \frac{1}{r_n^6}$$

Typical values of σ are 0.05-0.1 eV

For the quadrupolar glass $C(r) \propto 1/r^3$ and $\ln \mu \propto \gamma(T)E^{3/4}$

It is difficult to distinguish from the $E^{1/2}$ dependence.

Einstein relation

$$\mu = \frac{eD}{kT}$$

How this relation is modified in the situation where we have a significant dependence of the mobility (and diffusivity) on the electric field (this is the case of correlated disorder)? We in the isotropic medium certainly have *two different mobilities*: perpendicular and parallel to the field direction. How the Einstein relation should be modified? Well known modification for 1D case (P. E. Parris et al, PRE 56, 5295 (1997))

$$\frac{\partial v}{\partial E} = \frac{eD}{kT}$$

The new result is that this relation is valid for any Gaussian DOS, and not only for the correlation function $C(r) \propto 1/r$, as it was suggested earlier. The only possible linear generalization for the multidimensional case is

$$\sum_i \frac{\partial v_i}{\partial E_i} = \frac{e \sum_i D_{ii}}{kT} \quad \text{or} \quad D_{\parallel} + (d-1)D_{\perp} = \frac{kT}{e} \frac{\partial v}{\partial E}$$

in the proper coordinate system (with E and v directed along one of the coordinate axis). This relation does not hold (S.V. Novikov, PRE 98, 012128 (2018)).

Conclusion: in the general case of multidimensional charge carrier transport we have no valid Einstein relation.

Injection: general consideration

$$\phi = \text{const}$$



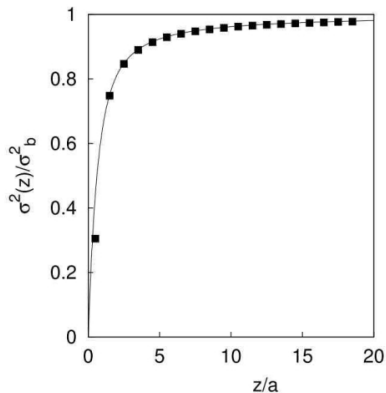
Boundary condition for the electrostatic potential at the electrode

$$\phi|_{\text{electrode}} = \text{const}$$

This means that at the electrode plane there is no electrostatic disorder at all ($\sigma = 0$), no matter how many dipoles (or quadrupoles) are situated in the bulk.

Magnitude of the electrostatic disorder decreases in the vicinity of the electrode.

Magnitude of the disorder at the interface



Novikov and Malliaras, PRB **73**, 033308 (2006)

Calculation of the magnitude of the dipolar disorder in the vicinity of the electrode

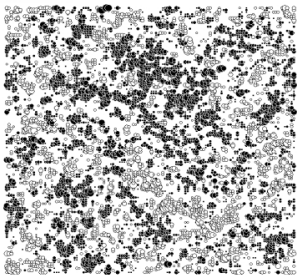
$$\sigma^2(z)/\sigma_b^2 = 1 - \frac{a_0}{2z} (1 - \exp(-z/a_0))$$

$$a_0 \approx 0.76a$$

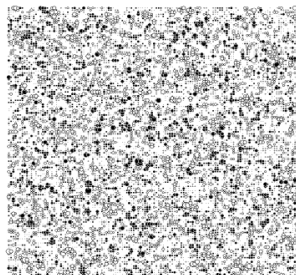
This leads to the decrease of the total injection current but the distribution of the current density becomes more homogeneous across the surface of the electrode.

At the very first layer of the organic material $\sigma_i^2/\sigma_b^2 = 0.3$.

Correlation properties: dipolar disorder



Disorder in the bulk $C(\mathbf{r}) \propto 1/r$



First organic layer at the electrode

$$C(z, z', \boldsymbol{\rho} - \boldsymbol{\rho}') = \langle U(z, \boldsymbol{\rho}) U(z', \boldsymbol{\rho}') \rangle \approx \begin{cases} \sigma_b^2 a_0 \left(\frac{1}{\rho} - \frac{1}{\sqrt{\rho^2 + 4z^2}} \right), & z = z' \\ \sigma_b^2 \frac{2a_0 z_1}{z_2^2 - z_1^2}, & \boldsymbol{\rho} - \boldsymbol{\rho}' = 0, \quad z_2 > z_1 \end{cases}$$

Novikov, phys. status. solidi (c) **5**, 750 (2008)

Injection current channeling

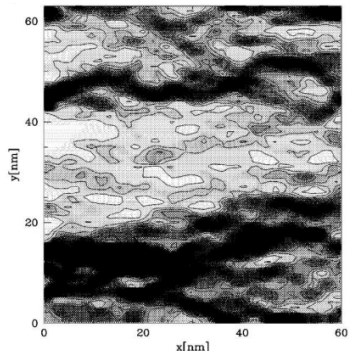


FIG. 3. The current density distribution along the direction of the field (x direction) for $F=0.5$ MV/cm. The dark parts on this contour plot correspond to regions with high current density. The

E. Tutis et al, PRB 70, 161202 (2004)

“Injection and strong current channeling in organic disordered media”

From the Abstract:

“The current density variations reach several orders of magnitude ...

The injection hot spots further induce current channels in the bulk of the material... this current channeling is expected to have a serious impact on device characteristic and performance.”

This calculation has been carried out not taking into account peculiarities of the electrostatic disorder at the interface.

Fortunately, this terrible picture does not describe real devices. Reduction of the magnitude of the energetic disorder and change of the correlation properties at the interface tremendously reduce channeling.

Bimolecular recombination (Paul Langevin)

Kinetics of bimolecular recombination $e^+ + e^- \rightarrow \emptyset$: $\frac{d(n,p)}{dt} = -\gamma np$

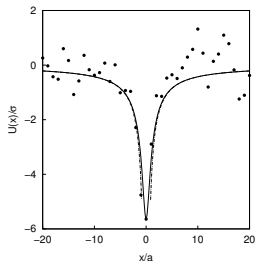
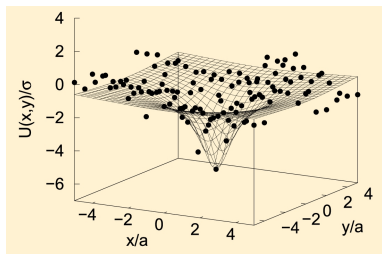
For the homogeneous medium without disorder Paul Langevin obtained

$$\gamma = \gamma_L = \frac{4\pi e}{\varepsilon} (\mu_+ + \mu_-)$$

P. Langevin, *Ann. Chim. Phys.* **28**, 433 (1903), the paper is actively cited until now.

Can we apply the conception of Langevin recombination to amorphous (and, hence, inhomogeneous) materials? Is γ still the same?

Electrostatic dipolar disorder: averaged energy of the fluctuation-arranged well



Why correlation is important for recombination? A simplified picture: low mobility carrier (let it be a hole) sits at the bottom of the potential well organized by the medium fluctuations and the fast electron is approaching. In the first approximation the electron feels the Coulomb attraction to the hole *and* the average fluctuation potential of the well (repulsive). Such potential is zero for the non-correlated medium.

Figure shows the two-dimensional cross-section of the energy in the vicinity of the hole (points show the actual values of energy at the different sites, surface shows the averaged profile).

One-dimensional cross-section near the deep trap; the solid line shows the function $-U_0 C(r)/\sigma^2$, and the broken line shows the plot for $-0.76U_0 a/r$, here U_0 is the depth of the trap.

Mean field approximation

We make a crucial approximation, by replacing the true fluctuating energy by the conditional average assuming that the one charge is sitting at the bottom of the well with depth U_0 . Thus we obtain the effective interaction between charges due to the effect of the random medium and calculate the recombination rate constant for the given U_0 . Then we make the averaging over U_0 .

For the Gaussian DOS the conditional average is

$$U_{fluct}(r) = -U_0 \frac{C(r)}{C(0)}, \quad U_{fluct}(0) = -U_0, \quad U_{fluct}(r \rightarrow \infty) = 0$$

The resulting averaged rate constant is

$$\langle \gamma \rangle = \frac{4\pi(D_+ + D_-)}{(2\pi\sigma^2)^{1/2}} \int_{-\infty}^{\infty} dU_0 \frac{\exp\left(-\frac{(U_0 - \langle U \rangle)^2}{2\sigma^2}\right)}{S(U_0)}, \quad \langle U \rangle = -\sigma^2/kT$$

$$S(U_0) = \int_R^{\infty} \frac{dr}{r^2} \exp\left(-\frac{e^2}{\epsilon r} - U_0 \frac{C(r)}{C(0)}\right)$$

Effective charge of the trapped carrier: dipole glass

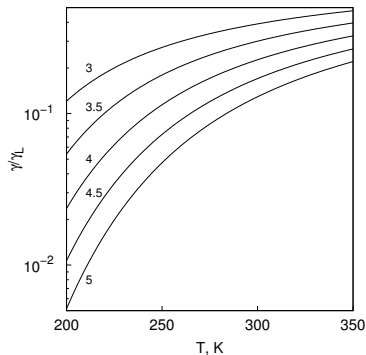
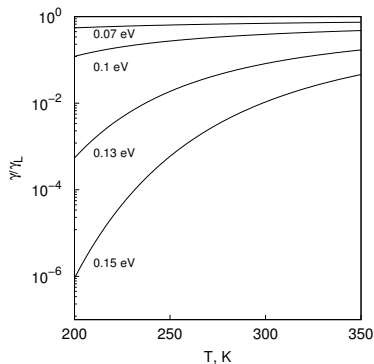
Interaction energy between approaching electron and the complex "trapped hole plus the well organized by the medium" for the dipole glass model is

$$U(\mathbf{r}) = -\frac{e^2}{\epsilon r} - U_0 \frac{C(\mathbf{r})}{C(0)} \simeq -\frac{e^2}{\epsilon r} - U_0 \frac{Aa}{r}$$

The effective charge of the hole is $e^* = e + U_0 \frac{Aa\epsilon}{e}$; for very deep traps ($U_0 \rightarrow -\infty$) $e < -U_0 \frac{Aa\epsilon}{e}$ the interaction between electron and hole becomes *repulsive*.

Naturally, the recombination becomes less effective in comparison with Langevin recombination. For low temperature the difference could be huge, $\gamma \ll \gamma_L$.

Magnitude of the suppression



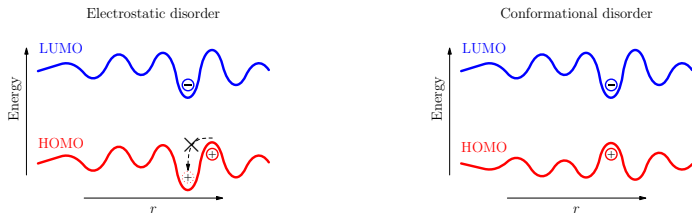
Bimolecular recombination rate constant in the dipolar glass, $\sigma \simeq 0.1$ eV is the rms disorder. (left) Lines show the ratio γ/γ_L for various values of σ , indicated near the corresponding curve. We assume $\epsilon = 3$ here. (right) Plot of the ratio γ/γ_L for various values of ϵ , indicated near the corresponding curve. Increase of ϵ is analogous to the increase of σ because it again strengthens effect of the disorder (we assume here $\sigma = 0.1$ eV).

Enhanced recombination: is it possible?

Reversed situation, i.e. the *enhanced* recombination with $\gamma > \gamma_L$ is possible in some amorphous semiconductors.



Conformational disorder as the "parallel" disorder



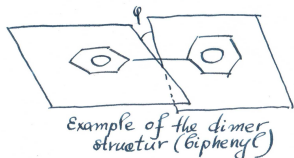
Computer simulation shows that in materials with molecules having significant permanent dipole or quadrupole moment the electrostatic contribution dominates in the total energetic disorder, while in other materials (Spiro-DPVBi) the conformational disorder is dominating (A. Massè et al, *Phys. Rev. B*, **95**, 115204 (2017)).

Conformational disorder could provide the "parallel" random energy landscape where HOMO and LUMO levels move in the opposite directions under variation of some disorder governing parameter, and, hence, the energy levels for electrons and holes move in the same direction giving the additional *attraction* between electron and hole resulting in $\gamma > \gamma_L$.

S.V. Novikov, *J. Phys. Chem. C* **122**, 22856 (2018)

Conformational disorder: dimer model

Conformationally-dominated disorder with the "parallel" random energy landscape could be quite common for materials built from spacious and asymmetric molecules.

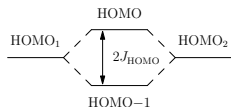
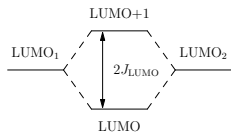


With variation of φ the transfer integral varies as

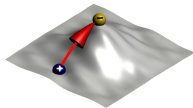
$$J \propto |\cos \varphi|$$

(A. Troisi, A. Shaw, *J. Phys. Chem. Lett.* **7**, 4689 (2016)) and HOMO and LUMO

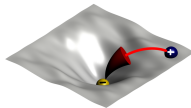
move in the proper way, as suggested by the simplest ZINDO estimation. Magnitude of the angle fluctuation should be $8^\circ - 15^\circ$ to provide reasonable values of σ .



Electrostatic disorder

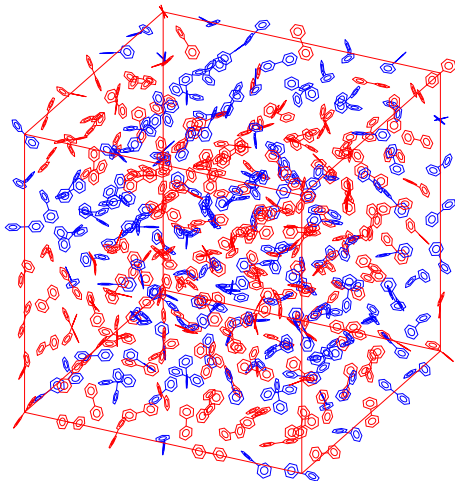


Conformational disorder



Random energy landscape for the moving carrier.

Conformational disorder: biphenyl glass

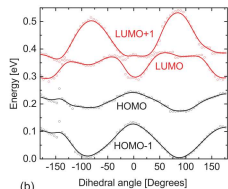
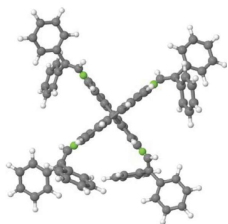


Blue and red molecules have the HOMO-LUMO gaps greater or smaller than the average gap.

Correlation of the dihedral angles naturally occurs due to steric interaction between molecules (packing).

Correlated conformational disorder (molecular scale simulation)

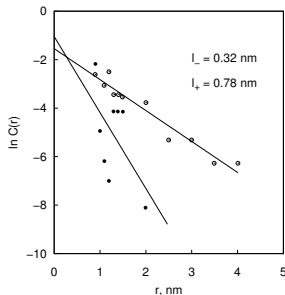
A. Masse et al, PRB **95**, 115204 (2017)



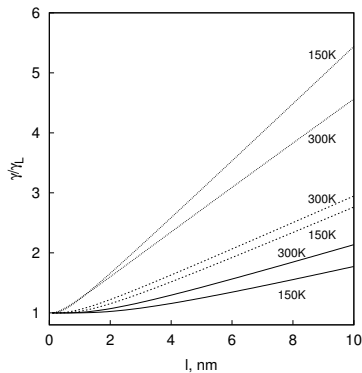
(b)

Three amorphous organic semiconductors have been studied. In two of them (α -NPD, TCTA) the electrostatic disorder is dominating, while in Spiro-DPVBi the parallel conformational disorder dominates. Dimer model indicates that this could be a typical case.

Correlation function $C(r) \propto \exp(-r/l)$



Estimation for the enhancement factor $\zeta = \gamma/\gamma_L$



Dependence of $\zeta(l)$ for 150K and 300K. Solid, broken, and dotted lines show the behavior for n equals to 1, 0.7, and 0.5, correspondingly. We assume $\varepsilon = 3$ and $\sigma = 0.1$ eV.

Analytic estimation for ζ and stretched exponential correlations $\ln C(r) \propto -(r/l)^n$

$$\zeta \simeq \frac{l}{R_{\text{Ons}}} \left\{ \ln \left[\left(\frac{\sigma}{kT} \right)^2 \frac{l}{R_{\text{Ons}}} \right] \right\}^{1/n},$$

where $R_{\text{Ons}} = e^2/\varepsilon kT$ is the Onsager radius; approximate linear dependence takes place.

$$\frac{\partial \zeta}{\partial T} \simeq \frac{\zeta}{T} \left[1 - \frac{1}{n \ln(T_0/T)} \right], \quad T_0 = l\varepsilon\sigma^2/ke^2$$

and for $T < T_0$, there is a tendency of the derivative becomes negative with the decrease of n , in the full agreement with the figure.

For Spiro-DPVBi $n \approx 1$, $l = 0.32$ nm (electrons), and $l = 0.78$ nm (holes) (estimated from A. Massè et al. paper).

Where we can expect the enhanced recombination?

Even modest increase in γ with all other factors being the same (and this is a very big "IF") could provide the comparable increase in the device efficiency for OLEDs. The importance of this possibility is difficult to overestimate.

Hence the question: where to search for the promising materials? What they are?

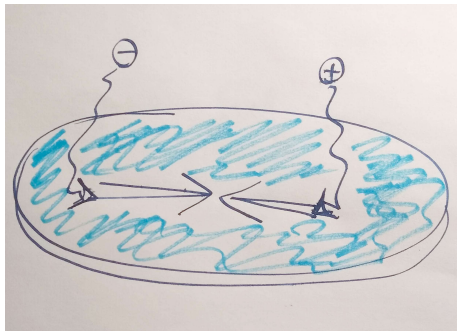
Necessary conditions:

- Absence of polar molecules which provide the electrostatic disorder. This means the minimal amount of nitrogen and oxygen atoms (none in the ideal case).
- Spatial correlation of the random energy landscape.
- Domination of the proper conformational disorder (the "parallel" random energy landscape).

Promising candidates are glassy liquid crystalline materials or macrocyclic aromatic hydrocarbons.

S.V. Novikov, J. Phys. Chem. C **123**, 18854 (2019)

2D recombination



Why 2D recombination?

Again about the kinetics of the bimolecular recombination (assuming the equal concentration of electrons and holes)

$$\frac{dn}{dt} = -\gamma n^2 \quad \Rightarrow \quad n(t) = \frac{n_0}{1 + \gamma n_0 t} \quad \Rightarrow \quad n(t) \propto t^{-1}, \quad t \rightarrow \infty$$

In poly- and oligo-thyphenes another kinetics is frequently observed

$$n(t) \propto t^{-b}, \quad b < 1$$

and formally we may describe it by

$$\frac{dn}{dt} = -\tilde{\gamma} n^{2+s}, \quad b = \frac{1}{1+s}$$

At the same time in such materials planar lamellar structures do exist with the thickness ≈ 1.5 nm having huge anisotropy of the mobility

$\frac{\mu_{\text{in plane}}}{\mu_{\text{out of plane}}} \simeq 100$ (H. Sirringhaus et al., Nature, 1999, 401, 685–688).

We assume that the recombination takes place in 2D lamellas, then the exponent $s > 0$ naturally occurs for the diffusion-limited kinetics.

Diffusion limited chemical reaction in low dimension

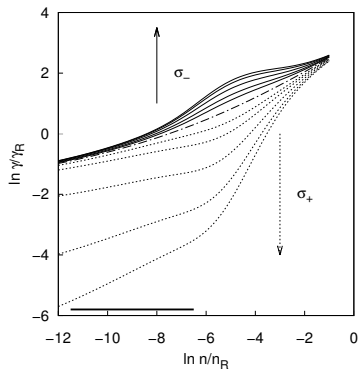
Traditional calculation of the rate constant of diffusion-controlled reactions means calculating it in a stationary state (assuming there is an inexhaustible source of material at infinity, which makes it possible to establish such a state). In this situation we can take the limit $n \rightarrow 0$ and calculate the true reaction rate constant.

In the stationary state the outflow of the material due to reaction is $\Delta_- \propto \gamma t$, and the maximal possible inflow is $\Delta_+ \propto (Dt)^{d/2}$, while for the development of the stationary state we need $\Delta_-/\Delta_+ \rightarrow 0$, hence it requires $d > 2$.

For $d \leq 2$ "the rate constant" goes to 0 for $n \rightarrow 0$ and may in the complex way (not by the power law) depend on n . The situation becomes even more complicated if we take into account the effect of disorder.

S.V. Novikov, Phys. Chem. Chem. Phys. **21**, 1174 (2020)

Dependence of "the rate constant" γ on concentration



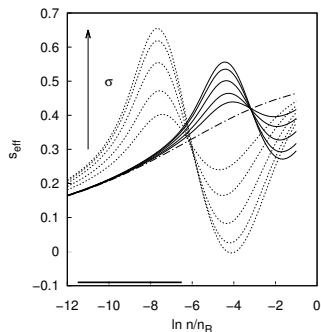
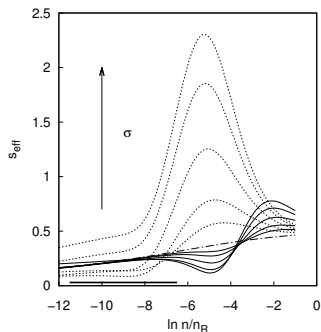
$$n_R = 1/\pi R^2$$

$$\gamma_R = 2\pi D$$

Here $R \simeq 1$ nm is the recombination radius, so n_R is the maximal concentration. Bold line at the abscissa axis shows the typical concentration diapason in experiments.

Dashed lines show the data for antiparallel (electrostatic) disorder, and solid lines show the data for the parallel conformational disorder with the amplitude from 0.05 eV to 0.15 eV and room temperature; line strokes with dots show the dependence in the absence of disorder. Correlation function is the exponential one with a correlation length of 5 nm.

Dependence of the effective exponent s_{eff} on n



$$s_{\text{eff}} = d \ln \gamma / d \ln n$$

The left picture is for antiparallel (electrostatic) disorder, the right picture is for parallel disorder with the amplitude from 0.05 eV to 0.15 eV, and room temperature. Spatial correlations are exponential, with a correlation length of 2 nm (continuous lines) or 10 nm (broken lines), dotted line show the result for the absence of disorder.

Conclusion

- Spatial correlation of the energy landscape is almost inevitable in amorphous organic semiconductors.
- Correlation could be of the electrostatic origin or conformational origin.
- Spatial correlation dictates the functional form of the drift mobility dependence on the electric field.
- In the vicinity of the injecting electrode the magnitude of the electrostatic disorder is reduced. Spatial correlation is much weaker in comparison with the bulk of the material.
- Spatial correlation of the energy landscape is the reason for deviation of the recombination rate constant from the Langevin value. For different kinds of disorder we may have the decrease or increase of the rate constant.

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Thank you for your attention!