

Charge carrier recombination in amorphous organic semiconductors

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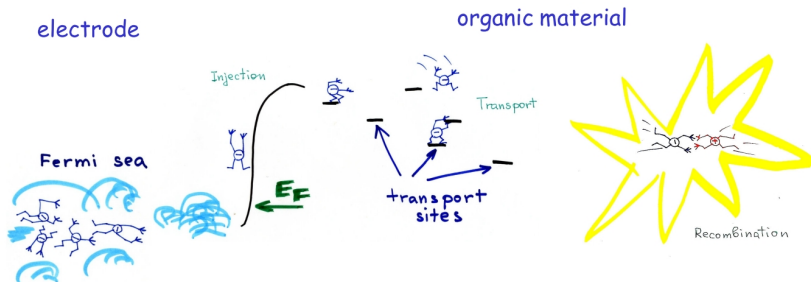
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- Recombination in amorphous organic semiconductors.
- Amorphous organic materials: general features of the random energy landscape.
- Electrostatic disorder: suppressed recombination.
- Conformational disorder: enhanced recombination.

Langevin recombination



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

For the homogeneous medium without disorder Paul Langevin obtained

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

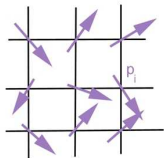
P. Langevin, *Ann. Chim. Phys.* **28**, 433 (1903), the paper is actively cited until now.

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

Electrostatic disorder: suppressed recombination

In many amorphous organic semiconductors $\gamma < \gamma_L$. Possible explanation is the mesoscopic separation of donors and acceptors. Such separation is favorable for photovoltaics and typically is specifically arranged in photovoltaic devices. Yet the suppressed recombination could occur in homogeneous organic semiconductors.

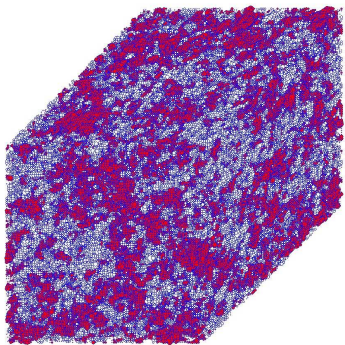
Let us consider the lattice model for the polar organic glass comprising of randomly oriented dipoles \mathbf{p}_i and the carrier energy $U(\mathbf{r})$ is dominated by the carrier-dipole interactions



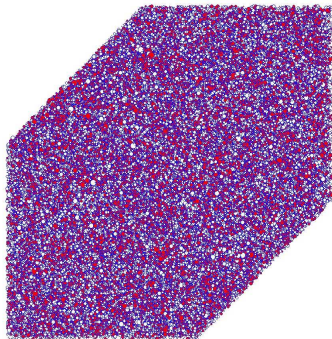
$$U(\mathbf{r}) = \sum_n \frac{e\mathbf{p}_n \cdot (\mathbf{r} - \mathbf{r}_n)}{\epsilon|\mathbf{r} - \mathbf{r}_n|^3}$$

Typically we get the Gaussian DOS $g(U) \propto \exp\left(-\frac{U^2}{2\sigma^2}\right)$, $\sigma \approx 2.35 \frac{epc^{1/2}}{\epsilon a^2}$, here a is the lattice constant (the distance between nearest neighbors), and $c \simeq 1$ is the fraction of occupied sites. Constant 2.35 is specific for simple cubic lattice; rms disorder $\sigma \simeq 0.1$ eV. In addition we have strong spatial correlation.

Long range spatial correlation in organic materials



Dipole glass



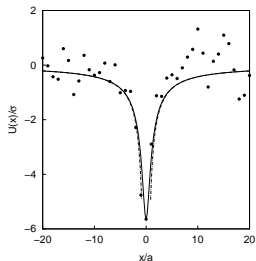
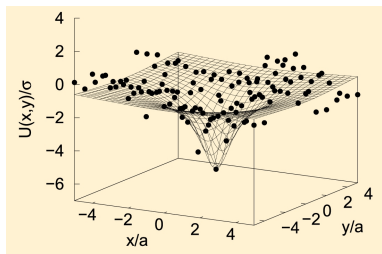
Non-correlated disorder

Balls of different colors show sites having different signs of the carrier energy U and the size of a ball is proportional to the absolute value of U . Reason for the correlation is the long range nature of the dipole potential.

Correlation function of the random energy (constant A depends on the details of the structure at short distance, $A = 0.76$ for the simple cubic lattice)

$$C(\mathbf{r}) \approx A\sigma^2 \frac{a}{r}, \quad r \gg a, \quad \text{in fact } r \simeq 2 - 3a \text{ is enough.}$$

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

We make a crucial approximation, by replacing the true energy by the conditional average assuming that the trapped hole is sitting at the bottom of the well with depth U_0 . Then we make the averaging over U_0 .

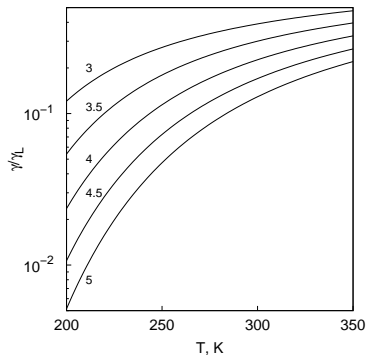
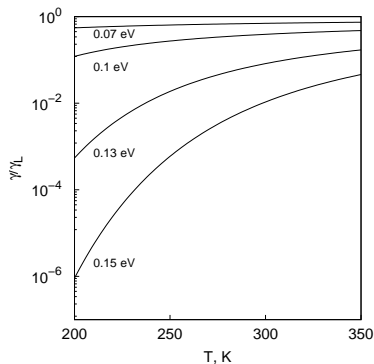
Interaction energy between approaching electron and the complex "trapped hole plus the well organized by the medium" is

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

The effective charge of the hole is $e^* = e - U_0 \frac{Aa\epsilon}{e}$; the deeper is the well, the smaller is the effective charge of the hole. For very deep traps $e < U_0 \frac{Aa\epsilon}{e}$ 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



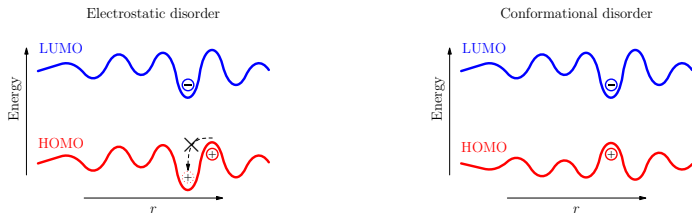
Bimolecular recombination rate constant in the dipolar glass, $\sigma \simeq 0.1$ eV is the rms disorder. (left) Lines show the ratio γ/γ_L for various values of σ , indicated near the corresponding curve. We assume $\epsilon = 3$ here. (right) Plot of the ratio γ/γ_L for various values of ϵ , indicated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

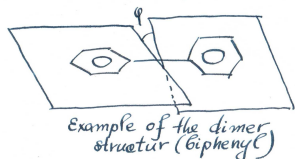


Large-scale computer simulation shows for the typical amorphous organic semiconductors that in materials with molecules having significant permanent dipole or quadrupole moment the electrostatic contribution dominates in the total energetic disorder, while in other materials (Spiro-DPVBi) the conformational disorder is dominating (A. Massè et al, *Phys. Rev. B*, **95**, 115204 (2017)). This is not surprising for the spiro-configuration.

Conformationally-dominated 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. Such disorder gives the additional *attraction* between electron and hole and results in the enhanced recombination with $\gamma > \gamma_L$.

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.

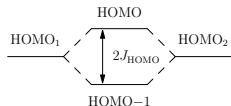
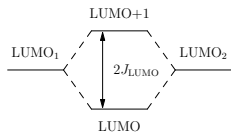


With variation of φ the transfer integral varies as

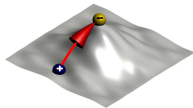
$$J \propto |\cos \varphi|$$

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

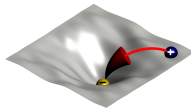
move in the proper way, as suggested by the simplest ZINDO estimation. Magnitude of the angle fluctuation should be $8^\circ - 15^\circ$ to provide reasonable values of σ .



Electrostatic disorder

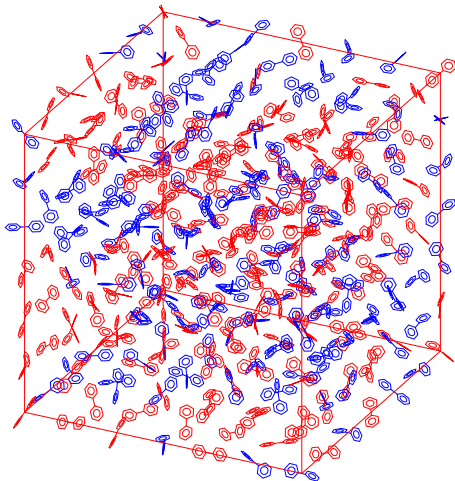


Conformational disorder



Random energy landscape for the moving carrier.

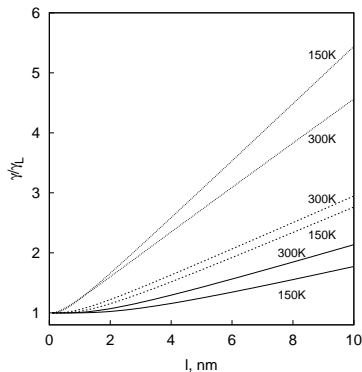
Conformational disorder: biphenyl glass



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).

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.

Conclusion

- Spatial correlation of the random energy landscape leads to the deviation of the recombination rate constant γ from the Langevin constant γ_L .
- Electrostatic disorder gives $\gamma < \gamma_L$, at low temperature even $\gamma \ll \gamma_L$.
- For the conformational disorder there is a general and quite typical possibility to arrange the landscape where $\gamma > \gamma_L$. For the reasonable estimation of relevant parameters we should expect the increase of γ by 50% – 100%.

- 1 S.V. Novikov, *Bimolecular Recombination of Charge Carriers in Polar Amorphous Organic Semiconductors: Effect of Spatial Correlation of the Random Energy Landscape*, J. Phys. Chem. C 2019, 122(40), 22856-22863.
- 2 S.V. Novikov, *Enhanced Bimolecular Recombination of Charge Carriers in Amorphous Organic Semiconductors: Overcoming the Langevin Limit*, J. Phys. Chem. C 2019, 123(31), 18854-18860.
- 3 S.V. Novikov, *Two-dimensional bimolecular recombination in amorphous organic semiconductors*, Phys. Chem. Chem. Phys. 2020, 22(31), 1174-1180.

Acknowledgements

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Thank you for your attention!