Simulation of charge transport in organic materials

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Max Planck Institute for Polymer Research

Japan-Germany joint workshop
Kyoto, 21-23 January 2009
Motivation

Charge transport simulations

Hexabenzocoronene derivatives

Max Planck Institute for Polymer Research

Max Planck Institute for Polymer Research

Location: Mainz, Germany. Founded 1983, 450-500 employees [ca 300 researchers]. Annual budget 24 Mio Euro, 330 papers/year. 6 departments (synth. chemistry, functional materials, theory and simulations, NMR, biomaterials, surfaces and interfaces)

Simulation of charge transport in organic materials
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Organic Electronics Group

Valentina Marcon
rational compound design
atomistic simulations of discotics:
HBC, perylene, trizigzag

Alexander Lukyanov
systematic coarse-graining
force-matching
Alq3, donor-acceptor polymers

Thorsten Vehoff
conducting polymers
organic crystals
atomistic force-fields

Victor Rühle
coarse-graining
large time- and length-scale simulations
conjugated polymers

www.mpip-mainz.mpg.de/~andrienk/

Simulation of charge transport in organic materials
Aims

To replace active inorganic layers in FETs, LEDs and solar cells with suitable organic films (OFETs, OLEDs, etc).

Requirements: high charge carrier mobilities (conjugated polymers, discotic LCs), controlled morphology (self-organizing materials).
12% efficiency solar cell having 1m² in a full sunlight at noon at the equator will produce 120 watts of peak power.

Primary task: improvement of efficiencies and life-times.
Only the excitons generated within 10 nm of the interface have a chance to dissociate, most excitons decay prior to dissociation.

Blend solar cell

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<th>Charge transport simulations</th>
<th>Hexabenzocoronene derivatives</th>
</tr>
</thead>
</table>

Blendsolar cell

**Competition between the interfacial area and the length of the percolation path**

Motivation

(1) excitons are generated close to the interface; (2) there are uninterrupted pathways to the electrodes; (3) the phases are connected exclusively to the appropriate electrode

**Structure-charge mobility relation**

1. self-organization and large scale morphology
2. electronic properties: bandgap, alignment of levels
3. local molecular arrangement and **charge transport**

How to combine quantum and classical descriptions?
Gaussian Disorder Model

Gaussian disorder model

Transition probability to hop from $i$ to $j$
(Miller and Abrahams, 1960)

$$\omega_{ij} = \begin{cases} 
\nu_0 \exp(-2\alpha r_{ij}) \exp \left( -\frac{\epsilon_j - \epsilon_i}{k_B T} \right), & \epsilon_j > \epsilon_i \\
\nu_0 \exp(-2\alpha r_{ij}), & \epsilon_j < \epsilon_i 
\end{cases}$$

Gaussian distribution of energies:

$$g_e(\epsilon) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left( -\frac{\epsilon^2}{2\sigma^2} \right)$$

Separations:

$$g_s(r_{ij}) = \frac{1}{\sqrt{2\pi}\Sigma} \exp \left( -\frac{r_{ij}^2}{2\Sigma^2} \right)$$

No analytical solution - Kinetic Monte Carlo simulations are fitted to some empirical function.

A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960)
GDM mobility

\[ \mu = \mu_0 \exp \left[ -\left( \frac{2\sigma}{3k_B T} \right)^2 \right] \times \exp \left[ C_0 \sqrt{F} \left( \left\{ \frac{\sigma}{k_B T} \right\}^2 - \Sigma^2 \right) \right] \]

- \( \mu_0 \) - mobility prefactor - related to the transfer integral \( J \)?
- \( \sigma \) - energetic disorder - related to conjugation length, electrostatic potential?
- \( \Sigma \) - positional disorder - related to hopping distance, orientation?

GDM parameters can **quantify** differences in charge transport of different materials, but offer no way to **predict** them from chemical and physical structure.

Force-field

\[ U = \sum_{\text{bonds}} \frac{1}{2} K_b (r - r_0)^2 \]

\[ + \sum_{\text{angles}} \frac{1}{2} K_\theta (\theta - \theta_0)^2 \]

\[ + \sum_{\text{dihedrals}} \sum_{n=1}^{3} \left[ \frac{V_n}{2} + \left( 1 + (-1)^{n+1} \cos n\phi \right) \right] \]

\[ + \sum_{\text{impropers}} K_d (\psi - \psi_0)^2 \]

\[ + \sum_{i} \sum_{j>i} \left[ \frac{1}{4\pi \varepsilon \varepsilon_0} \frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \right] \]

Goal: to match calorimetric, X-ray scattering, and NMR data.
Systematic coarse-graining

**Bonded interactions**  The coarse-grained potential is a Boltzmann inversion of the corresponding probability density distribution. It is computed via Monte Carlo sampling of the atomistic structure of an isolated molecule.

\[
P(\{x_1, x_2, \ldots, x_N\}) = \prod_{i=1}^{N} P(x_i).\
\]

\[
P(x_i) \sim \exp \left( - \frac{U(x_i)}{k_B T} \right).
\]

**The non-bonded potential**  Can be found by fitting RDFs for bonded interactions (iterative Boltzmann or force-matching)

\[
U_{cg}^{nb} = \sum U_{ij}(r_{ij}).
\]

---


Marcus rates

\[ \omega_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k T}} \exp \left[ -\frac{(\Delta G_{ij} - \lambda)^2}{4 \lambda k T} \right] \]

\( \lambda \) - reorganization energy

\( J_{ij} = \langle \psi^i | \mathcal{H} | \psi^j \rangle \) - transfer integral

\( \Delta G_{ij} = E \cdot r + \Delta G_{ij}^{el} \) - free energy difference between initial and final states

R. A. Marcus, Rev. Mod. Phys. 65, 599 (1993)
Reorganization Energy - typical values

\[ \omega_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k T}} \exp \left[ -\frac{(\Delta G_{ij} - \lambda)^2}{4\lambda k T} \right] \]

Table: Internal reorganization energies of typical discotics.

Geometry optimisation B3LYP/6-311++g(d,p).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda ), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>triphenylene</td>
<td>0.18</td>
</tr>
<tr>
<td>hexabenzocorononene</td>
<td>0.1</td>
</tr>
<tr>
<td>triangular PAH</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Transfer Integral $J$

\[ \omega_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k T}} \exp \left[ -\frac{(\Delta G_{ij} - \lambda)^2}{4\lambda k T} \right] \]

Energetic disorder (electrostatics and polarization)

Along the normal the $\pi$ electrons form a linear quadrupole and the molecule is far less polarizable than in the molecular plane.

$$\omega_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda kT}} \exp \left[ -\frac{(\Delta G_{ij} - \lambda)^2}{4\lambda kT} \right]$$

**Electrostatic case** [interaction of a linear quadrupole $Q$ with a charge]

$$\Delta G_{\text{el}} = \frac{3eQ}{16\pi\epsilon_0 r_{12}^3} (\cos^2 \theta_1 - \cos^2 \theta_2)$$

**Polarization case** [interaction of a charge with a polarizable dipole, $\alpha = 0.7\text{Å}^3$]

$$\Delta G_{\text{pol}} = \alpha \left( \frac{e}{4\pi\epsilon_0 r_{12}^2} \right)^2 (\sin^4 \theta_1 - \sin^4 \theta_2)$$

Only **out-of-plane** fluctuations contribute to energetic disorder.
Disorder is intrinsically greater for negative charges than for positive ones.

KMC simulations of time-of-flight experiments

- inject a charge
- pick a neighboring site \( j \) at random, weighting by its rate \( \omega_{ij} \)
- advance waiting time by \( t_i = \frac{-\log \xi}{\sum_{j=0}^{N} \omega_{ij}} \), where \( \xi \) is a random number.

Derivatives of hexabenzocoronene

Influence of chemical structure and morphology on the charge carrier mobility?

Hexabenzocoronene derivatives

Side chain dependence


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Temperature dependence

Herringbone phase has better azimuthal register of molecules


Distributions of Transfer Integrals

Frequency plots of the logarithm of the transfer integral squared. a) herringbone (300 K) and hexagonal (400 K) phases of the systems with C\textsubscript{12} side chains. b) herringbone (320 K) and hexagonal (400 K) of HBC with dove-tail side chains.

Motivation

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Hexabenzocoronene derivatives

Hexabenzocoronene

Collaboration with the organic chemistry group...

"So much for prediction but what about reality!"
Motivation

Charge transport simulations

Hexabenzocoronene derivatives

Discotic liquid crystals

Triphenylenes, hexabenzocoronenes, phthalocyanines ...

A. M. van de Graats et al, Advanced Materials 1999
L. Schmidt-Mende et al, Science 2001
H. J. Räder et. al. Nat. Mat. 2006
M. Van der Auweraer, F. C. De Schryver Nat. Mat. 2006
Maximum of the transfer integral (hoping rate) is in the face-to-face geometry and in a 60 deg twisted arrangement of neighbors.
Triangularly-shaped PAH

Compound design

- Triangularly-shaped core

Triangularly-shaped PAH

Compound design

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- The core can provide 60 deg twist, due to steric repulsion

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- Bulky side groups - to lock the azimuthal rotation

**Compound design**

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- Side chains to make the compound soluble

Compound design

- Triangularly-shaped core
- The core can provide 60 deg twist, due to steric repulsion
- Bulky side groups - to lock the azimuthal rotation
- Side chains to make the compound soluble
- Polar side chains - to further stabilize the twist

Motivation

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Hexabenzocoronene derivatives

X-Ray structures

Experimental data

X. Feng, W. Pisula, and K. Mülлен - synthesis and characterization

Motivation

Charge transport simulations

Hexabenzocoronene derivatives

MD simulations

Simulations

Distribution functions of the azimuthal angle and transfer integral between nearest neighbors.

Motivation
Charge transport simulations
Hexabenzocoronene derivatives

Triangular-shaped PAH

PR-TRMC mobility

PR-TRMC mobilities vs temperature

V. Marcon (MPIP)
F. Grozema (TU Delft)

Summary and software package

csgth.mpi-p-mainz.mpg.de

C++, test suite, svn, wiki, bug tracker
Collaborations and financial support

- V. Marcon, V. Rühle, T. Vehoff, A. Lukiyanov, K. Kremer
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