'Bottom-up' modelling of charge transport in soft materials

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Outline

1. Introduction
2. Charge transport in polymer semiconductors
3. Conformational disorder
4. Conclusions and outlook
Acknowledgements

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Computers

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Soft materials

- Organic semiconductors
  - crystalline organics (e.g. pentacene)
  - polymer semiconductors
  - liquid crystals
- Large-area/flexible electronic devices
  - displays
  - lighting
  - photovoltaics
Soft materials

• Compared to inorganic materials, organic electronics have the potential to tailor-make compounds for diverse applications
  • we can make any material we want BUT
• Relationship between structure and property (charge mobility) not known
  • we don’t know what we want to make
Top-down modelling

- Device physics

1. Assume transport model (e.g. GDM)
   - number of free parameters

2. Fit parameters to experimental measurements

3. Calculate charge mobility using KMC/Master equation
   - No clear relationship between molecular structure and model parameters
     - not predictive
   - Instead of imposing a transport model from above, use theory to study systems in microscopic detail and infer charge transport behaviour
     - bottom-up modelling
Molecular modelling of organic electronics

- Charge transport
  - quantum chemistry/solid-state physics
  - large sizes of molecules often necessitates use of lower order theory (semi-empirical) or DFT
- Organic materials are soft
  - bound by weak van der Waals interactions
  - (classical) molecular simulations - soft matter
- Combined classical and quantum methods
  - use MD snapshots for QC calculations
  - develop simplified (semi-classical) models
1 Introduction

2 Charge transport in polymer semiconductors
   MD simulations
   Transport model
   Transfer integrals

3 Conformational disorder

4 Conclusions and outlook
Polymer semiconductors

- Polymers have been investigated as active elements for over 60 years
  - first devices (TFTs) demonstrated early 90’s
- P3HT *de facto* standard polymer semiconductor
  - conjugated backbone
  - flexible sidechains

Poly(3-hexylthiophene)
What do we know about P3HT

- Crystalline P3HT forms well-defined lamellar structure
  - high degree of structural order

- Electronic properties described by disordered models
  - charge transport described by hopping models
  - optical properties: polaron models

- Where is the disorder?
• Classical MD simulations of crystalline P3HT
  • 12 chains, 40 rings per chain

• Marcon-Raos/OPLS forcefield
• Anisotropic-\textit{NPT} MD simulations
• Simulation lengths up to 5 ns
  • multiple short simulations (0.3-1 ns)

\( T = 100 \, \text{K} \)

\( T = 300 \, \text{K} \)
Microstructure & dynamics

- Crystalline order preserved (until 500 K)\(^1\)
- Unremarkable dihedral angle distributions
  - insufficient to cause localization
- Long range order in the dihedrals
- Dynamic disorder not important
- Signs of static disorder

\(^1\)DLC, D. P. McMahon, & A. Troisi, *JPCB*, 2009
Charge carrier wavefunction

- Quantum chemical calculations reveal long lived traps
  - HOMO density (from AM1 calculations) at different times

\[ t_1 \quad t_2 \]

\[ \text{Density} \]

\[ 0.25 \quad 0.2 \quad 0.15 \quad 0.1 \quad 0.05 \quad 0.0 \]

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \quad 30 \quad 35 \]

\[ 0 \quad 10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \quad 70 \quad 80 \quad 90 \quad 100 \]

\[ \text{Time (ps)} \]

\[ \text{Monomer} \]

\[ 2 \text{DLC, D. P. McMahon, \& A. Troisi, JACS, 2009} \]
Classification of states

- States classified by...
  - localization
  - time dependence

- persistent (29%), non-persistent, double (or more) persistent
Where does it trap?

- Localized traps
  - HOMO localized on planar segments

- Trap depth $> k_B T$
  - $E_{\text{HOMO}} - E_{\text{HOMO-1}}$
    - localized: $0.104 \pm 0.046$ eV
    - non-localized: $0.046 \pm 0.031$ eV
What about polarons?

- Charge localized by static disorder further localized by electron-phonon coupling

- In P3HT both deformations are co-operative - molecular planarized by excess charge
Density of states

• Missing link between microscopic and device modelling

• Edge fit by double Gaussian
  • width of dominant Gaussian $\approx 0.1$ eV
Possible transport mechanisms

1. Hopping between localized states (Variable Range Hopping)
2. Excitation from localized to delocalized state (Mobility edge)
3. Charge-carrier moves with distortion (Pseudo-polaron)
Towards the mobility

- Charge transfer rates $k_{CT}$ are key determinants of the charge mobility
- Using Marcus-Hush approximation

$$k_{CT} = \frac{2\pi}{\hbar^2} t^2 \sqrt{\frac{1}{4\lambda\pi k_B T}} \exp \left[ -\frac{(\Delta G + \lambda)^2}{4\lambda k_B T} \right]$$

- $t$ transfer integral
  - may be determined from QC calculations

$$t = \langle \phi_i^0 | F^0 | \phi_j^0 \rangle$$

- DFT - B3LYP/6-31G*
- Consider charge transfer between thiophene rings
Along the chain

- Distribution of intrachain transfer integrals
  
  HOMO/HOMO, HOMO/HOMO-1, HOMO-1/HOMO, HOMO-1/HOMO-1
  
  100 K (left), 300 K (right)

- HOMO/HOMO transfer integral very much larger than the others ($\approx 1.10 \text{ eV}$)
Between chains

- Interchain transfer integrals
  - $\bar{t}(r)$: average transfer integral between rings of separation $r$

- $t$ generally decreases with distance
  - peak in HOMO-1/HOMO-1, HOMO/HOMO-1, HOMO-1/HOMO transfer integrals at $r \approx 5$ Å
Beyond GDM

- Non-monotonic behaviour of transfer integrals not seen in models such as GDM
  - Strong coupling between ring separation and orientations
    \[ p_1(r) = \langle u_1 \cdot u_2 \rangle_r \]

- Close approach between S and C-C bond on rings on adjacent chains (overlap of HOMO-1)
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3 Conformational disorder
   Liquid crystal semiconductors
   Transition from dynamic to static disorder

4 Conclusions and outlook
Dynamic and static disorder

- Localization may occur due to static disorder
  - grain boundaries
  - chmical defects
- Organic materials bound by 'soft’ van der Waals forces
  - disorder induced by thermal motion [Fratini’s talk this morning]
Dynamic disorder in molecular crystals

- Thermal motion in organic crystals leads to fluctuations in intermolecular transfer integrals\(^3\)

- Develop simple (semi-classical) model of charge carrier motion in organic crystals\(^4\)

\(^3\) A. Troisi & G. Orlandi, *JPCA*, 2006
\(^4\) A. Troisi & G. Orlandi, *PRL*, 2006
Liquid crystal semiconductors

- Between dynamic and static disorder
  - thermal motion - fluctuations in positions of neighbouring molecules
  - column breaks
- Computational characterisation (D. Andrienko, MPI Mainz)
  - broad distribution of transfer integrals\(^5\)
  - transfer integral fluctuations
- Many degrees of freedom per molecule

\(^5\) J. Kirkpartick et al, PRL, 2007
Model

- Extend model used for crystals
  - use Langevin instead of harmonic oscillators

\[ m\ddot{u}_i = -ku_i - \gamma \dot{u}_i(t) + R(t) + \frac{\partial}{\partial u_i} \langle \psi(t) \mid H_{el}(t) \mid \psi(t) \rangle \]

- Complex dynamics of transfer integral can be reproduced by model with three Langevin oscillators\(^6\)

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\(^6\) A. Troisi, DLC, & D. Andrienko, *PRL*, 2009
Charge mobility

- Numerically integrate equations of motion

\[ \mu = 2.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \]

- No \textit{a priori} assumptions or fitting parameters

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7 A. Troisi, DLC, & D. Andrienko, \textit{PRL}, 2009
From molecular crystals to polymers

- Increasing $\gamma$ leads to transition from dynamic to static disorder\(^8\)
  - DOS independent of $\gamma$

- Time evolution of wavefunction

\(^8\) A. Troisi & DLC, *JCP*, 2009
Properties of the transition

- Scaling mobility by temperature$^9$

$^9$A. Troisi & DLC, *JCP*, 2009
Conclusions

• Combination of classical and quantum modelling provides a powerful method for the study of the charge transport in ‘soft’ materials
  • interplay of nuclear and electronic degrees of freedom
  • disorder - dynamic and static
• Polymer semiconductors
  • combination of MD/QC calculations used to infer charge transport mechanism
  • transfer integrals calculated from MD trajectories show more complex distributions than assumed in charge transport models
• Effect of dynamic and static disorder on charge transport
  • develop simple, predictive model for the study of charge transport in soft materials
  • works across parameter range modelling organic crystals to polymers/DNA
• Bottom-up modelling, from molecular to device scale

Classical MD

Quantum chemistry

Localization
DOS
Transfer rates

Quantum Dynamics

Coarse-grained simulations

Device modelling
(e.g. Kinetic MC, master equation)