Multiscale Modelling of Electronic Transport Through Organic Materials

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Simulation for Nanoscale Structure & Function
Outline

- Organic Electronics, Organic Light Emitting Diodes: an Intro
- Why Nanoscale, Electronic Transport and/or Multiscale Modeling?
- MMM@HPC Project
  - Details of implementation
  - Multiscale Simulation of OLED in Steps
    - Morphology
    - Local Electronic Structure
    - Charge Transport
  - Polymer Wrapping of Carbon Nanotubes
- Conclusions / Future Work
Modelling Organic Thin Film Materials

- Industrial applications involving nanoscale materials already exist:
  - OLED
  - Organic Photo Voltaics
  - Organic electronics

- Problem with efficiency, lifetime and manufacturing:
  - Printable Materials?

- Hopping transport through *disordered* material
Multiscale Simulation Steps: OLED

**STEP 1**
- Morphology

**STEP 2**
- Local Electronic Structure

**STEP 3**
- Charge Transport

MACROSCOPIC PROPERTIES
Multiscale Simulation Steps: OLED

**STEP 1**
- **MACROSCOPIC PROPERTIES**
  - MORPHOLOGY
    - KIT

**STEP 2**
- **LOCAL ELECTRONIC STRUCTURE**
  - BASF / Univ. Mons

**STEP 3**
- **CHARGE TRANSPORT**
  - Imperial College London

**MACROSCOPIC PROPERTIES**
Could scripting, SSH, PBS, etc. be replaced with something more automatic and *clickable*?
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Issues to address:

- Reusability
- Data Complexity
- Licensing issues
- Security & Reliability
- Capacity & Capability
Could scripting, SSH, PBS, etc. be replaced with something more automatic and clickable?

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MMM@HPC: Can we meet these challenges?

**Reusability**
- GridBeans
- UNICORE Workflows

**Data complexity**
- Chemical Mark-up Language (CML)
- OpenMoIGRID

**Solution for licensing issues**
- UNICORE: UVOS/SAML/VOMS
- Open Source Licenses

**Security & Reliability**
- UNICORE
- Grid Security Infrastructure (GSI)

**Capacity & Capability**
- High Performance Computing (PRACE)
- Distributed resources (D-Grid, EGI)

**YES!**
What is UNICORE?

- UNICORE: UNiform Interface to COmputing Resources
- Grid computing technology (grid middleware) supported by EMI
- Seamless, secure, and intuitive access to distributed grid resources
- Used in daily production at several supercomputer centres worldwide
- Open source under BSD license
- Implements standards from the Open Grid Forum (OGF)

A. Streit et al., UNICORE 6 - Recent and Future Advancements, Annals of Telecommunications 65 (11-12), 757-762 (2010).
Application interfaces: GridBeans

- Provide a way to use scientific application on HPC resources by non experts
- Designed to decouple scientific applications from the underlying (changing) grid protocols (UNICORE, Globus, Portals)
  - Different simulation workflows re-use the same GridBean
  - Different GridBeans can be employed for the same workflow step
UNICORE Rich Client and Workflows

UNICORE Client layer

Portal client, e.g., GridSphere
command-line client
Eclipse-based client

DEPOSIT GridBean GUI

UNICORE Rich Client

Workflow

Embedded visualisation with Jmol
Control flow: Example
Data Flow: Example
OLED Workflow

Simulation protocol

QM: Geometry Optimization

MM: Film deposition

MM: Determination of Site pairs

QM: Pairwise QM calculations J (eV), DE (eV)

CG: Compute Charge mobility

FEA: Calculate Current Density

1 Molecule

CML

MOPAC GridBean

CML

DEPOSIT GridBean

PDB

n Molecules

BABEL GridBean

CML

Pairfinder GridBean

CML

PairwiseQM GridBean

CML

Reduction GridBean

CML

Edge

Lean Workflow
Realization: GridBeans and Workflow

Tackle data complexity

- Chemical Markup Language (CML)

- OpenMoI GRID library with MMM@HPC extensions
  Provides:
  - Chemical file format convertors
  - An extendable data model
  - Manage dataflow
  - Application wrapper (next slide)

- Further data models are being evaluated
Application Wrapper Lifecycle:
1. **Pre-processing**: Validation of App. Parameter, generation of app. specific input files
2. **Execution**: Run Apps in separate Processes, monitoring of stdout/stderr (allows interaction with the application)
3. **Post-processing**: Error Handling, Parsing App Output, Creation of Workflow Data
Multiscale Simulation Steps: OLED

STEP 1
- MORPHOLOGY

STEP 2
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STEP 3
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MACROSCOPIC PROPERTIES
Electronic structure, transport mechanism and disorder

Microscopic picture

Energy

EA

„CB“

„local EA“

DOS

„local IP“

IP

„VB“

Gasphase crystalline solid amorphous solid

Electronic structure, transport mechanism and disorder
Morphology

STEP 1

MORPHOLOGY
- Molecular modelling
  - DEPOSIT (Monte Carlo)
  - Coarse Grained Molecular Dynamics

STEP 2

LOCAL ELECTRONIC STRUCTURE
- Quantum chemistry
  - Turbomole (DFT)
  - Mopac (semi-empirical)

STEP 3

CHARGE TRANSPORT
- Kinetic Monte Carlo
  - ToFeT
  - Analytic

MACROSCOPIC PROPERTIES
A single molecule is pre-optimised on QM level

Rigid body approximation

Depositing molecules individually using Metropolis Monte Carlo scheme

Partially deposited film is “frozen”

Simulated Annealing taken as a good approximation to the global optimum

Z-potential drives molecules towards partially deposited film

2D periodic boundary conditions
DEPOSIT Test: Alq3 Morphology

computed density: 1.24 g/cm³

literature value: 1.3 g/cm³

P. M. Borsenberger and D. S. Weiss, Organic Photoreceptors for Xerography (Marcel Dekker, New York, 1998)

MD Approach: D. Adrienko, JCTC 7, 3335 (2011)
Local Electronic Structure

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**MACROSCOPIC PROPERTIES**
Electronic Structure: Hopping Rates

Estimating Marcus’ hopping rate with (DFT) Turbomole or semiempirical methods (MOPAC)

\[ \Gamma_{if} = \frac{2 \pi}{\hbar} |J_{if}|^2 \frac{1}{(4 \pi \lambda k_B T)^{1/2}} \exp\left(-\frac{(\lambda + \Delta E)^2}{4 \lambda k_B T}\right) \]

R. A. Marcus, Rev. Mod. Phys. 65, 599 (1993)

\( J_{if} \) of a molecular dimer is estimated as (frozen orbital approx.):

\[ J_{if} \approx < \Phi_i^M | H_{KS}^D | \Phi_f^M > \]

Or:

\[ J_{if} \approx \frac{H_{if} - \frac{1}{2}(H_{ii} + H_{ff})S_{if}}{1 - S_{if}^2} \]

V. Stehr, et al, PRB 83 155208 (2011)
Electronic Structure: Energy Disorder

- Energy disorder simulated with molecular static dipoles, or partial charges
- Functional quantum fragment model under testing
- State of the art in the field:
  - Difference between the frontier orbitals (alone)
    - C. Lee et al, JCTC, 7, 2556 (2011)
  - Classical approaches including electrostatics, van der Waals interaction, polarization, etc.
    - A. Fuchs et al, BASF, PCCP 14, 4259 (2012)
  - Static polarisation model gives $\Delta \sigma = 0.34$ eV agrees well with literature (V. Rühle, et al JTCT 2011)
Charge Transport

STEP 1

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  • Analytic

MACROSCOPIC PROPERTIES
Charge Transport: ToFeT

\[ \mu = \frac{\langle v \rangle}{F} \]

\[ \frac{\mu_e}{\mu_h} \approx 10^2 \]


Analytic solution to the master equation approach in preparation
Sorting CNT by selective polymer wrapping

- Four different polymers
  - P1: C_{12}H_{25}C_{12}H_{25}, X=N, Y=CH or X=CH, Y=N
  - P2: C_{12}H_{25}C_{12}H_{25}
  - P3: C_{12}H_{25}C_{12}H_{25}
  - P4: C_6H_{17}, C_6H_{13}

- Selectivity not fully understood
- MD inefficient to wrap the NTs
- No design principles

Coarse-grained model for conformational search

- MD inefficient
- Construct a geometrical coarse-grained model
  - Disk-joint model
  - Parametrisation of shapes and chemically constrained angles $\delta$ and $\gamma$ to polymer specific values by DFT

Polymer specific model for the internal energy (DFT): use dihedrals $\alpha$ and $\beta$ as free parameters.
Construction of conformational ensemble by recursive exhaustive sampling

Construct *all conformations* of polymers with length $n=12$ links, such that all polymer units (red discs) are in contact with the tube of a given diameter $D$.

For many diameters/polymer combinations no solutions exist!

Optimise the total internal energy: compute fraction of conformations with lowest internal energy.
Selective polymer wrapping of SW-CNT

Normalised relative intensity, exp.

Fraction of low energy solutions, theo.
Selective polymer wrapping of SW-CNT

P1 & P2: Fraction of solutions correlates with measured relative intensity!

No solutions! P3 does not wrap small tubes!

Many solutions for small radii

Normalised relative intensity, exp.

Fraction of low energy solutions, theo.
Selective polymer wrapping of SW-CNT

P1 & P2: Fraction of solutions correlates with measured relative intensity!

No solutions! P3 does not wrap small tubes!

Many solutions for small radii:

To do: refine the coarse-grained model with MD (multiscale)

Normalised relative intensity, exp.
Fraction of low energy solutions, theo.
Conclusions

- MMM@HPC Project develops a general framework for the type of calculations we are interested in.

- A multiscale simulation scheme was presented comprising:
  - Morphology
    - Deposit
  - Local electronic structure
    - DFT estimated Marcus’ hopping rates
    - Static dipole representation of energy disorder
  - Charge transport
    - ToFeT

- Geometrical coarse-grained model: while it correlates with experimental data, it still needs further improvements.
Future Work

- Further developing and refining the multiscale workflow, e.g. introducing feedback from QM back to morphology, guest-host systems, etc.

- Full integration of all the steps/codes into the GridBean/Unicore framework

- Streamlining the workflows making them useful for non-experts, goal: widening HPC and/or materials modelling user base
Team at KIT

Institute of Nanotechnology (INT)
- Pascal Friederich  OLED, Shredder code
- Franz Symalla  OLED, excited states interactions
- Tobias Neumann  Morphologies, DEPOSIT code
- Igor Beljakov  Graphene based devices, Intercalation
- Simon Widmaier  OLED, Morphologies
- Denis Danilov  Morphologies, Organic interfaces
- Wolfgang Wenzel

Steinbuch Centre for Computing (SCC)
- Angela Poschlad  Polymer wrapping of CNT, OLED
- Stefan Bozic  Workflow generation, Grid-beans
- Ivan Kondov  Workflow, UNICORE, HTC
THANK YOU!

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OLED (KIT) workflow in action