A numerical study of charge mobility in thin films of fullerene derivatives

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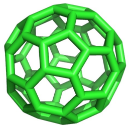
Background

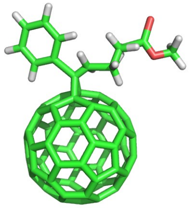
- Fullerene (C60) derivatives are a very important group of organic semiconductors for solar cells, thin film transistors and other applications.

- C60 has high electron and hole mobilities. (~1cm^2/Vs)
- Good electron acceptor

- Fullerene is often functionalised by the addition of side chains to:
  - Improve solubility (processability)
  - Optimize energy levels (for device operation)



C60



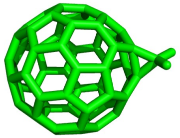
PCBM

Adv. Funct. Mater. 2009, 19, 779–788

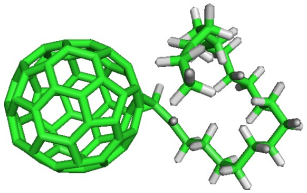
Introduction to the problem

- However, the addition of side chains change:
  1) The **separation** and **relative orientation** of molecules
  2) The **molecular packing** will be altered
  3) This alters the intermolecular charge transfer rates
  4) Thus **mobility will be altered**

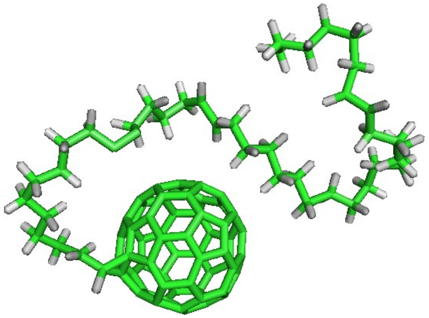
- This work examines the impact **side chain length** has on **mobility**.



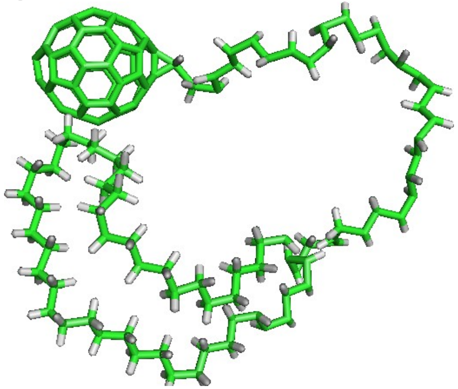
C60 with no chain



C60 with chain length 20



C60 with chain length 40



C60 with chain length 80

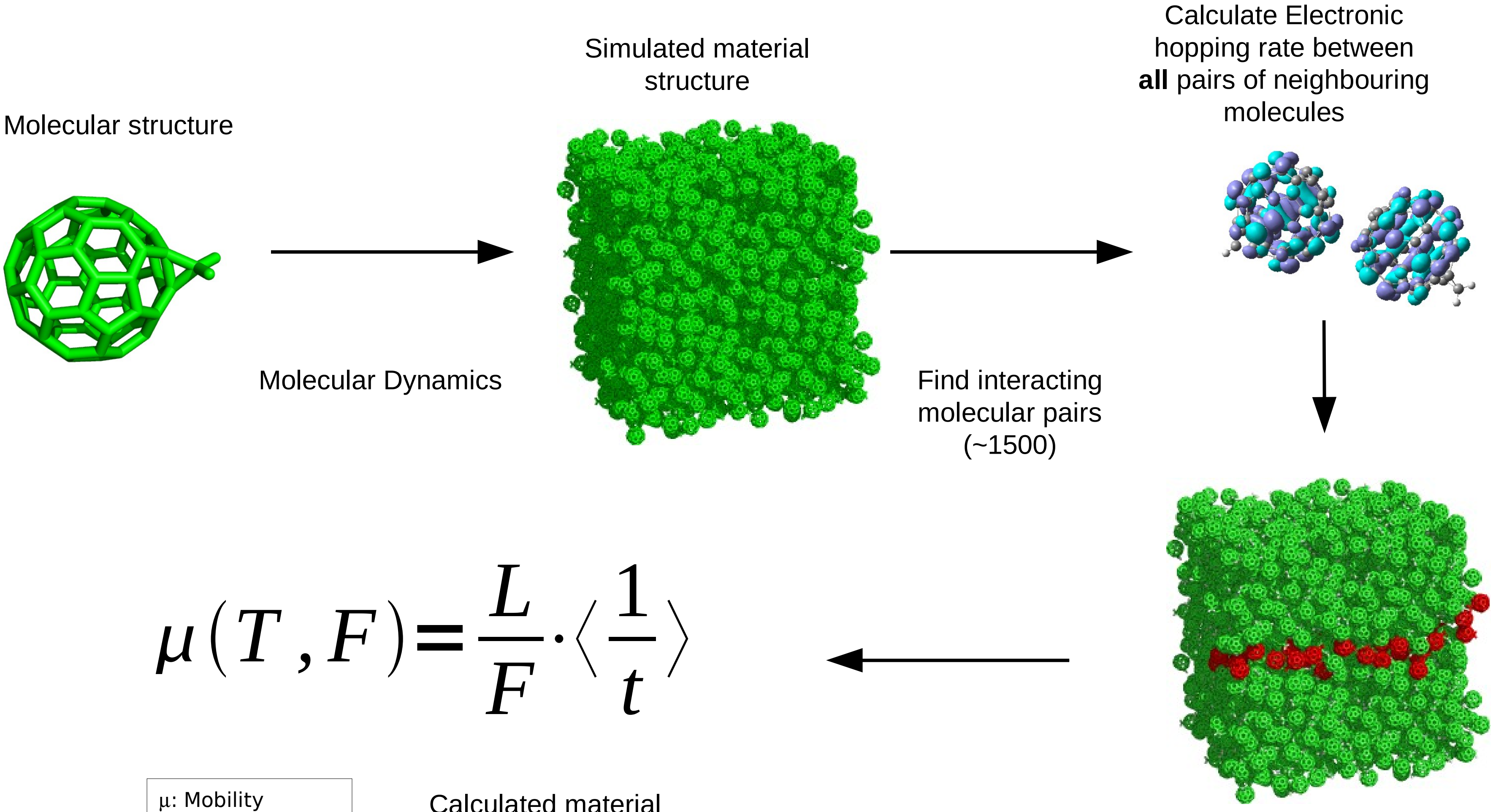
- We provides useful guidelines for design of new molecules.

Presentation outline

- Calculation of mobility
    - Simulation of a realistic material morphology with molecular dynamics.
    - Calculation of interaction energy of neighbouring molecules
    - Time of flight (Monte-Carlo) calculation of mobility

- Conclusions

Simulation process outline



Molecular structure

Molecular Dynamics

Simulated material structure

Find interacting molecular pairs (~1500)

Calculate Electronic hopping rate between **all** pairs of neighbouring molecules

Perform time of flight (Monte-Carlo) simulations

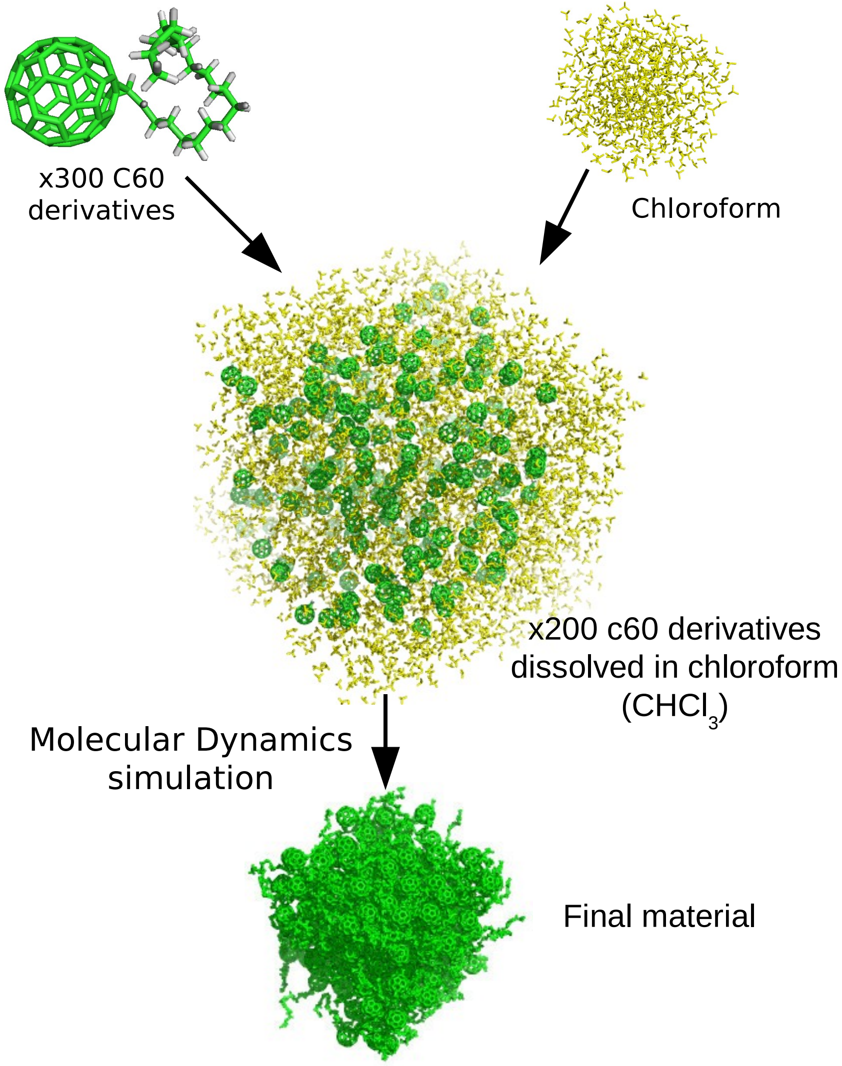
$$\mu(T,F)=\frac{L}{F}\cdot\left\langle\frac{1}{t}\right\rangle$$

Calculated material Mobility

μ: Mobility
L: Sample length
F: Electric field
t: Time of flight

Molecular dynamics:
Packing the simulation box

- To generate a reasonable morphology:
    - 300 fullerene molecules are placed in chloroform.
    - Atmospheric pressure is applied (100 kPa).
    - Solvent is gradually removed.
    - Thus **evaporation is simulated**
- This results in a realistic simulation of **solvent casting**.



x300 C60
derivatives

Chloroform

x200 c60 derivatives
dissolved in chloroform
$(CHCl_3)$

Molecular Dynamics
simulation

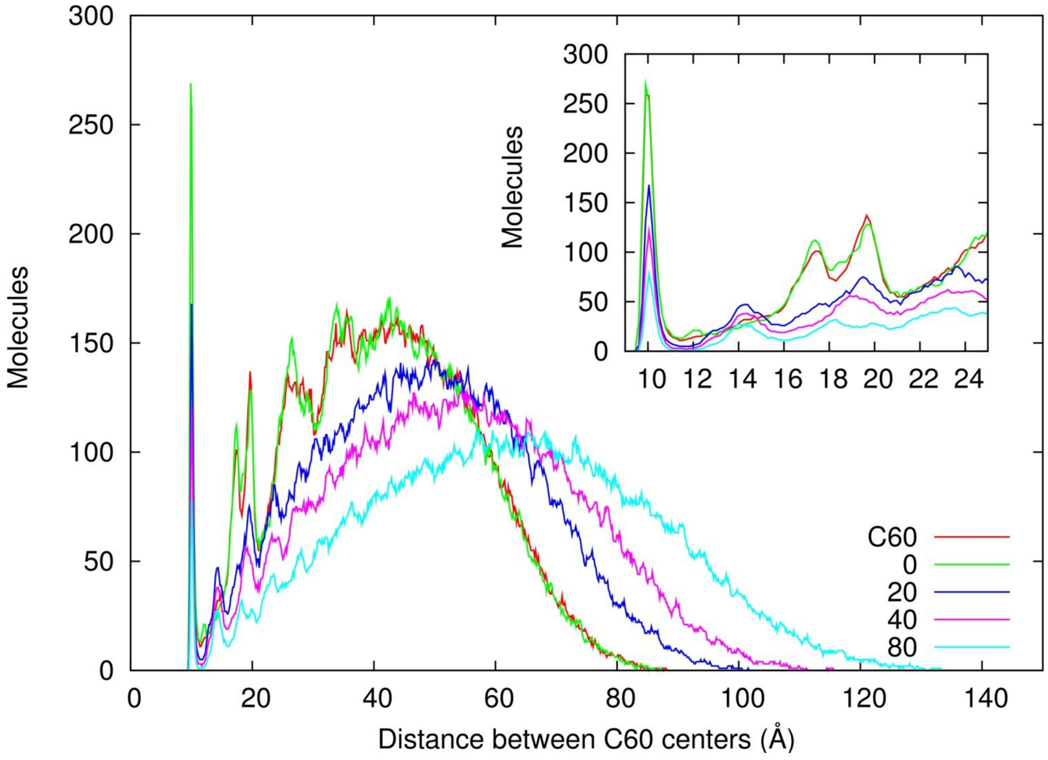
Final material

MD Results:
Molecular separation – C60 center separation

- 10Å nearest neighbour peak is observed – this is consistent with experiment.
  - The longer the chain the lower the peak.
  - ➢ The side-chain increases molecular separation of the nearest neighbour C60s.

- As chain length increases the average separation of molecules increases – the tail becomes more spread out.

- As chain length increases the range of molecular separation increases.



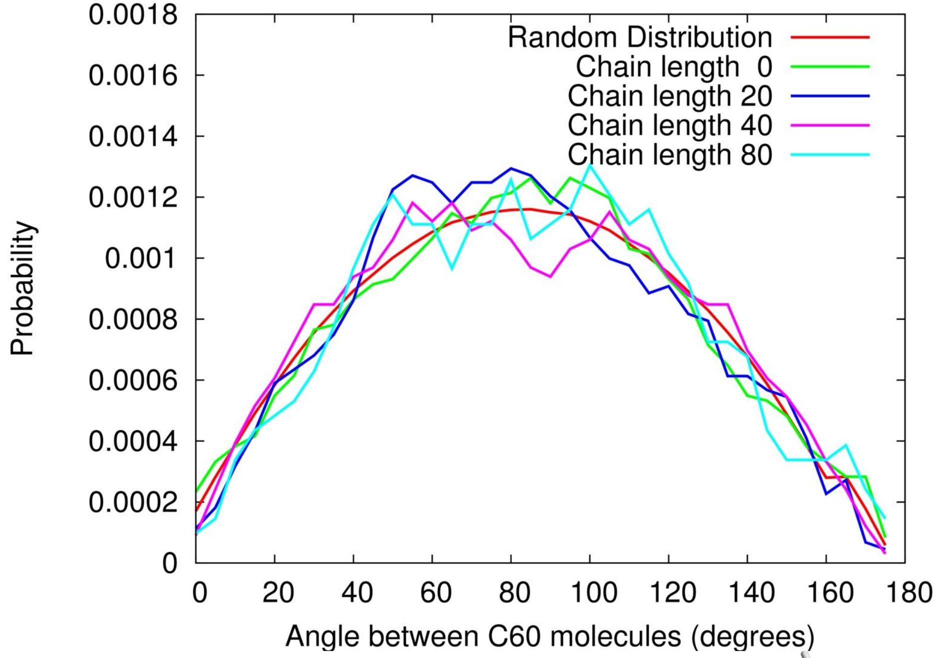
Histogram of C60 separation with in a box of 200 molecules.

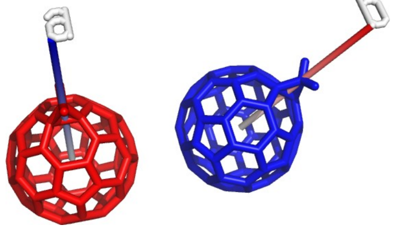
MD Results: Molecular packing – angle of separation

- Angle between the center of the C60 and the methano bridge is not dependent the upon chain length

- Angular distribution distribution matches that of a random distribution of C60s with a methano bridge very closely

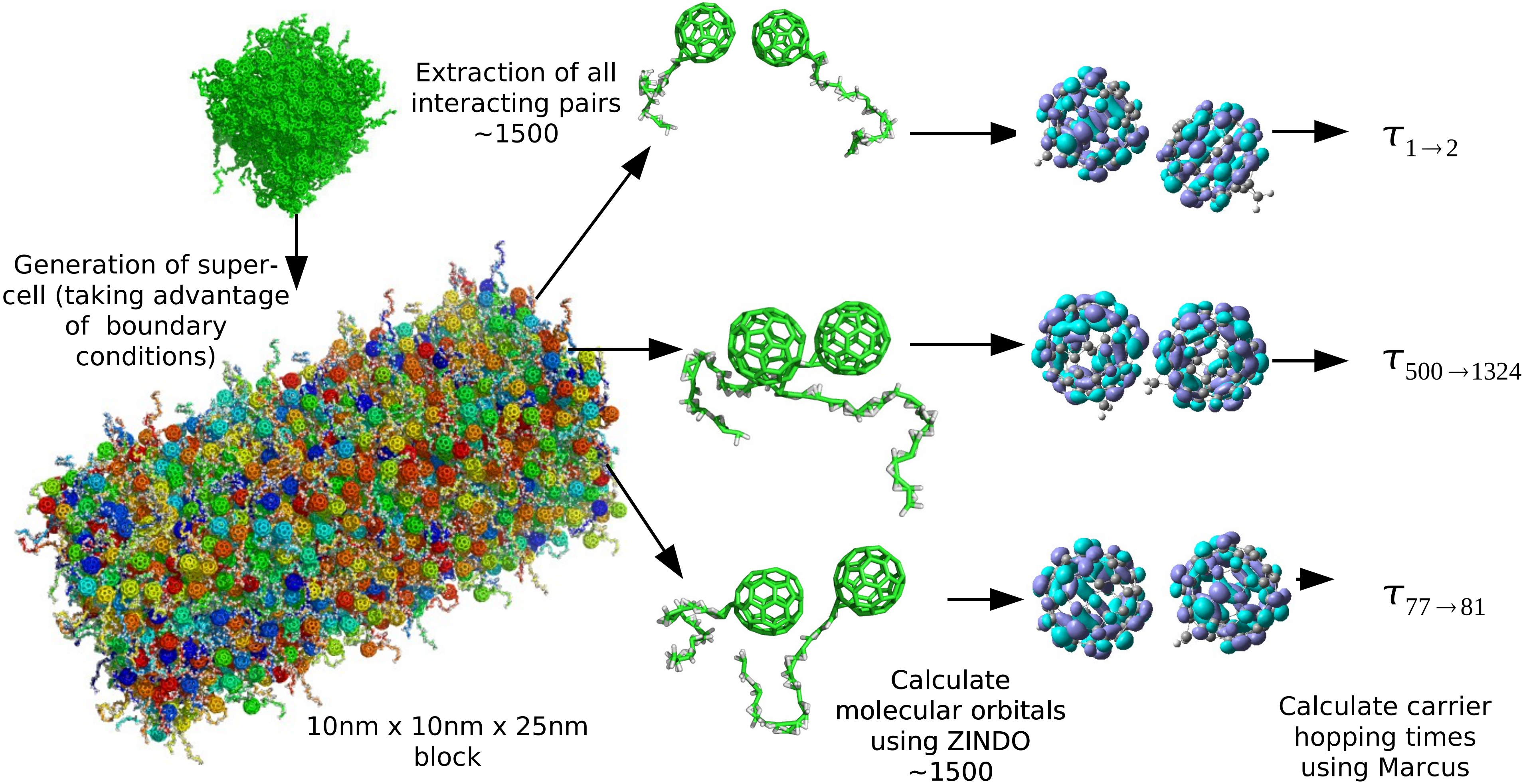
- This suggests the presence of the methano bridge and the chain does not cause increased angular ordering in the material.





Angle plotted is $\cos^{-1}(\mathbf{a}.\mathbf{b}/(|\mathbf{a}||\mathbf{b}|))$

Calculation of carrier hopping times



Generation of super-cell (taking advantage of boundary conditions)

Extraction of all interacting pairs ~1500

$\tau_{1 \rightarrow 2}$

$\tau_{500 \rightarrow 1324}$

$\tau_{77 \rightarrow 81}$

10nm x 10nm x 25nm block

Calculate molecular orbitals using ZINDO ~1500 calculations

Calculate carrier hopping times using Marcus Theory

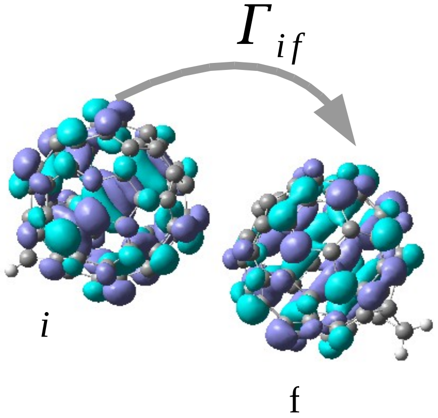
- Super-cell reduces impact of diffusion current

Calculation of hopping rate and Semi-classical Marcus Theory

- The molecular structure has been calculated
- The intermolecular electron transfer need to be calculated
- For this Semi-classical Marcus Theory is used

$$\Gamma_{if}=2\pi|J_{if}^{2}|(4\pi\lambda\kappa_{B}T)^{-\frac{1}{2}}\exp\left(-\frac{(\Delta E+\lambda)^{2}}{4\lambda\kappa_{B}T}\right)$$

Marcus's carrier transfer equation



Chem. Rev. 2004, 104, pp. 4971-5003

Transfer integral J

$$J_{if}=\langle\phi_i|H_e|\phi_f\rangle$$

Driving force ΔE

$$\Delta\epsilon=\langle\phi_f|H_e|\phi_f\rangle-\langle\phi_i|H_e|\phi_i\rangle$$

$$\Delta E=\Delta\epsilon+q(\boldsymbol{r}\cdot\boldsymbol{F})$$

Parameters

λ Reorganization energy
T temperature
κ_B Boltzmann’s constant

DFT, ZINDO/S, accuracy and speed 1

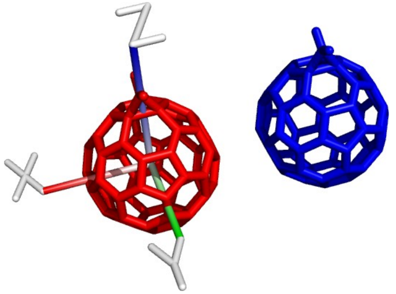
- Each simulation requires **~1500 hopping rate** calculations

- DFT (*Ab initio*) requires **~20hrs** of CPU time **per** C60 pair
  - Accurate prediction of J
    - However requires **~3.5years** of CPU time

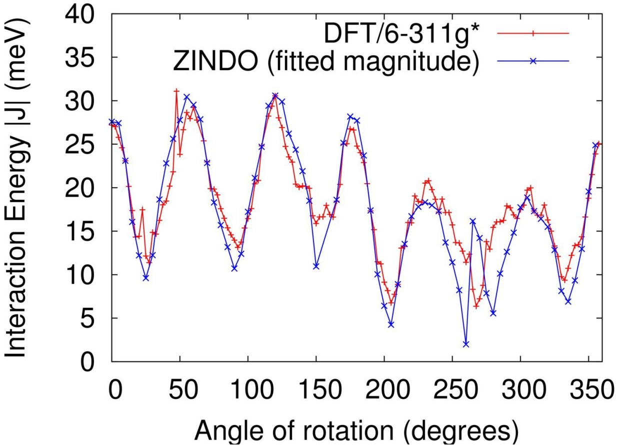
- ZINDO/S (*Semi-empirical*) requires **~4min** of CPU time **per** C60 pair
  - Predicts the **relative amplitude of J correctly**.
  - However, **underestimates J** the absolute magnitude
    - Takes only ~**4 days** of CPU time

- Solution:
  - Fit the magnitude of the ZINDO/S calculated J to DFT calculated J
  - How good is this approximation?

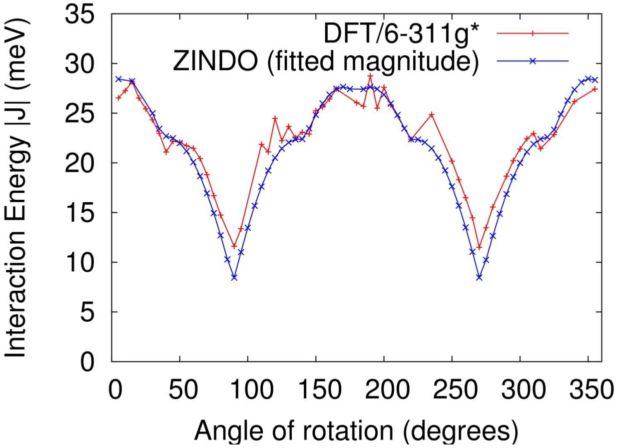
DFT, ZINDO/S, accuracy and speed 2



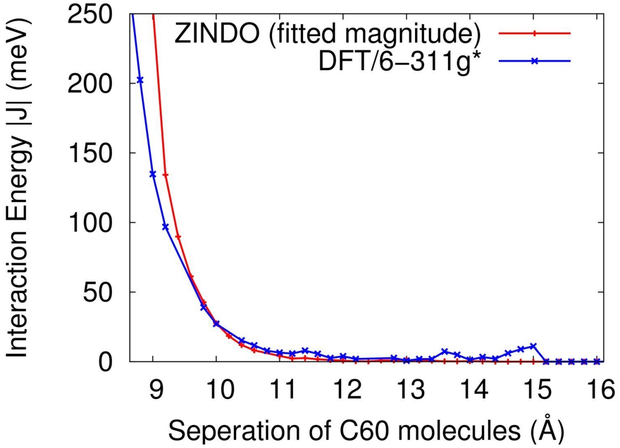
- Recall, there is a 10Å peak in the C60 separation plot
- The probability of C60 getting closer than 10Å is low
- After 10Å the interaction energy reduces very quickly



Rotation around y axis
at 10Å separation.



Rotation around x axis
at 10Å separation.

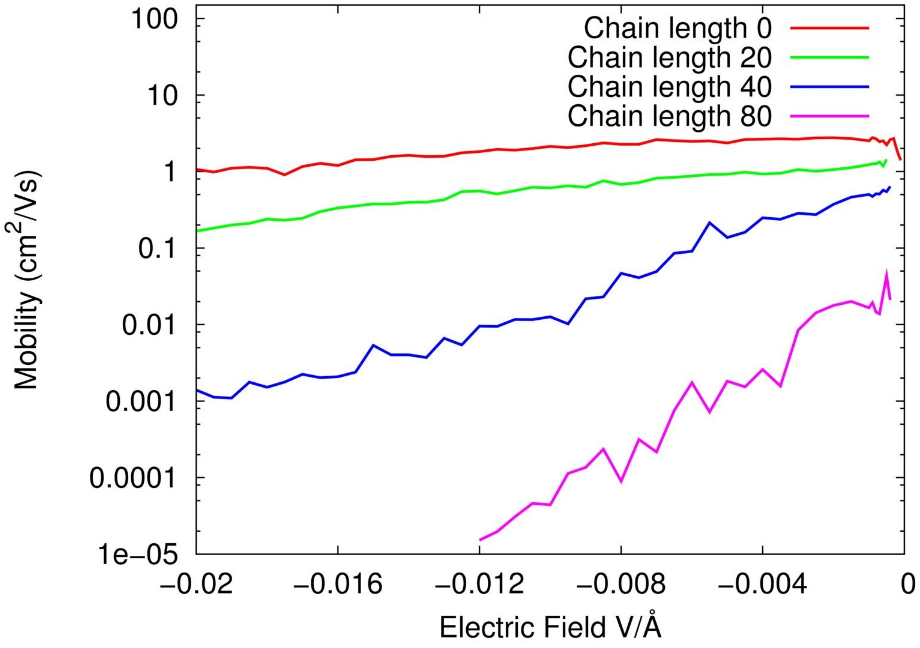


Displacement along x
axis

- Making this correction would seem reasonable
- The above DFT data points took **0.6 years** of computer time to generate, ZINDO/S calculations took **only 17 hrs**

Monte Carlo simulations of electron mobility

- At very low fields the mobilities appear to be the same.
    - Due to diffusion effects
- The longer the chain length the lower the mobility at high field.
    - C60 molecules pushed further apart by chain.
- As electric field increases the mobility decreases



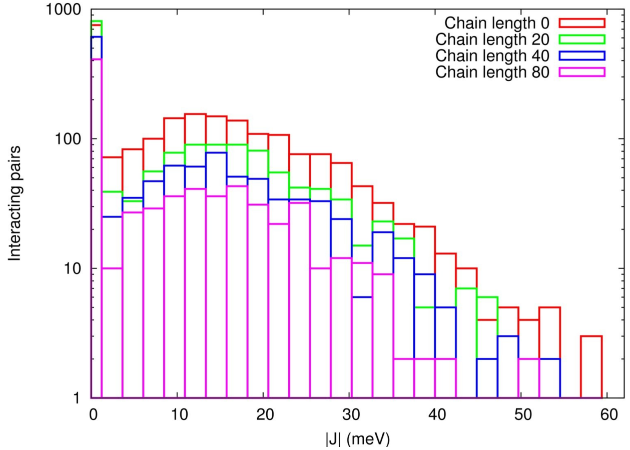
Mobility plot of the four systems at 300K

Monte Carlo simulations performed using open source ToFeT: http://tofet.org

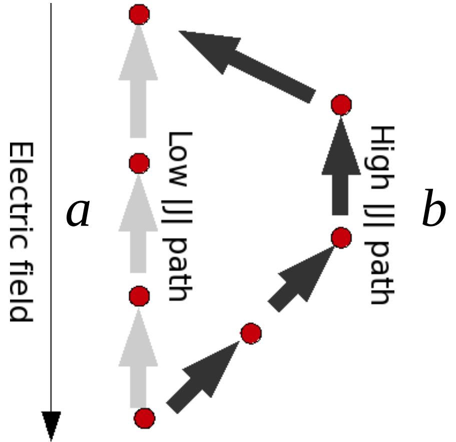
Explanation for decrease of mobility with field

- A wide distribution of transfer integral energies produces many carrier paths through the material.

- Consider, two paths through the material.
- *a)* A direct slow path parallel to the field
- *b)* A long quick path not parallel to the field.
- At low fields the electrons will travel quickly along path *b*, thus material mobility will be high.
- However, at high field carriers will have to execute a jump against the field – this is less probable so mobility will be lower.



Energy histogram of interacting pairs generated for a box of 200 molecules

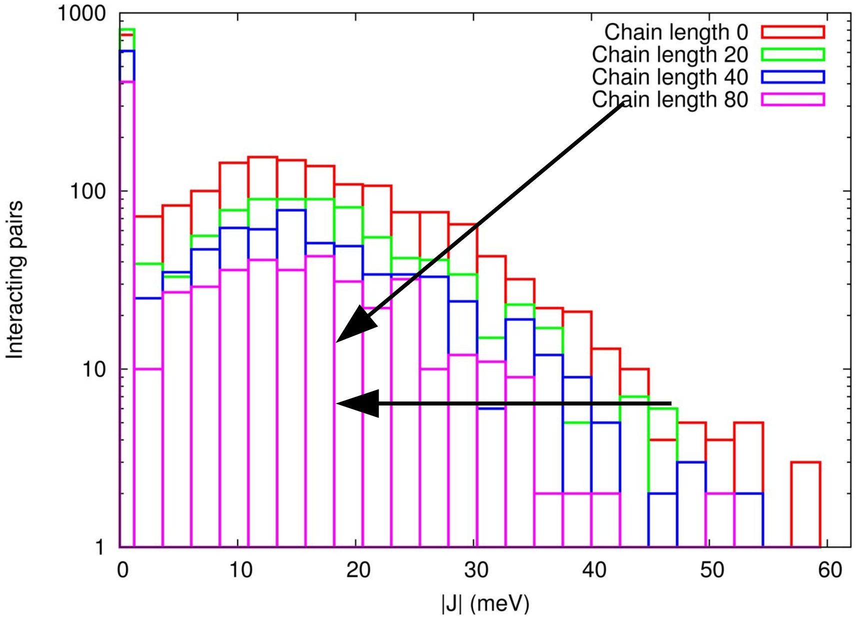


Motion of negative charge vi a low J path parallel to the field, and along a high J path non parallel to the field [1]

[1] H. Bässler phys. Stat. Sol. (b) **175**, 15 (1993)

Interaction energy |J| as a function of chain length

- As chain length increases the number interacting pairs decreases.
- As chain length increases the width of the distribution decreases.
- This is due to the chains pushing the C60 centers apart, coupled with the very fast roll-off of the interaction energy as a function of distance.



Energy histogram of interacting pairs generated for a box of 200 molecules

Conclusions

- Packing
    - The addition of a side chain disrupts the optimal packing of the C60 molecules
        - The longer the chain the more the 10Å peak is reduced.
        - The longer the chain the more the peak is reduced
    - Chain length nor the presence of the methano bridge affects the orientation of the C60 molecules.

Conclusions

- Interaction energy
  - ZINDO/S can be used to calculate the basis functions
    - |J| must be corrected through fitting

  - As chain length increases
    - The number of electronically interacting molecules decreases
    - The peak interaction energy also decreases

- Mobility
  - As the chain length is increased mobility decreases
  - As electric filed is increased mobility decreases

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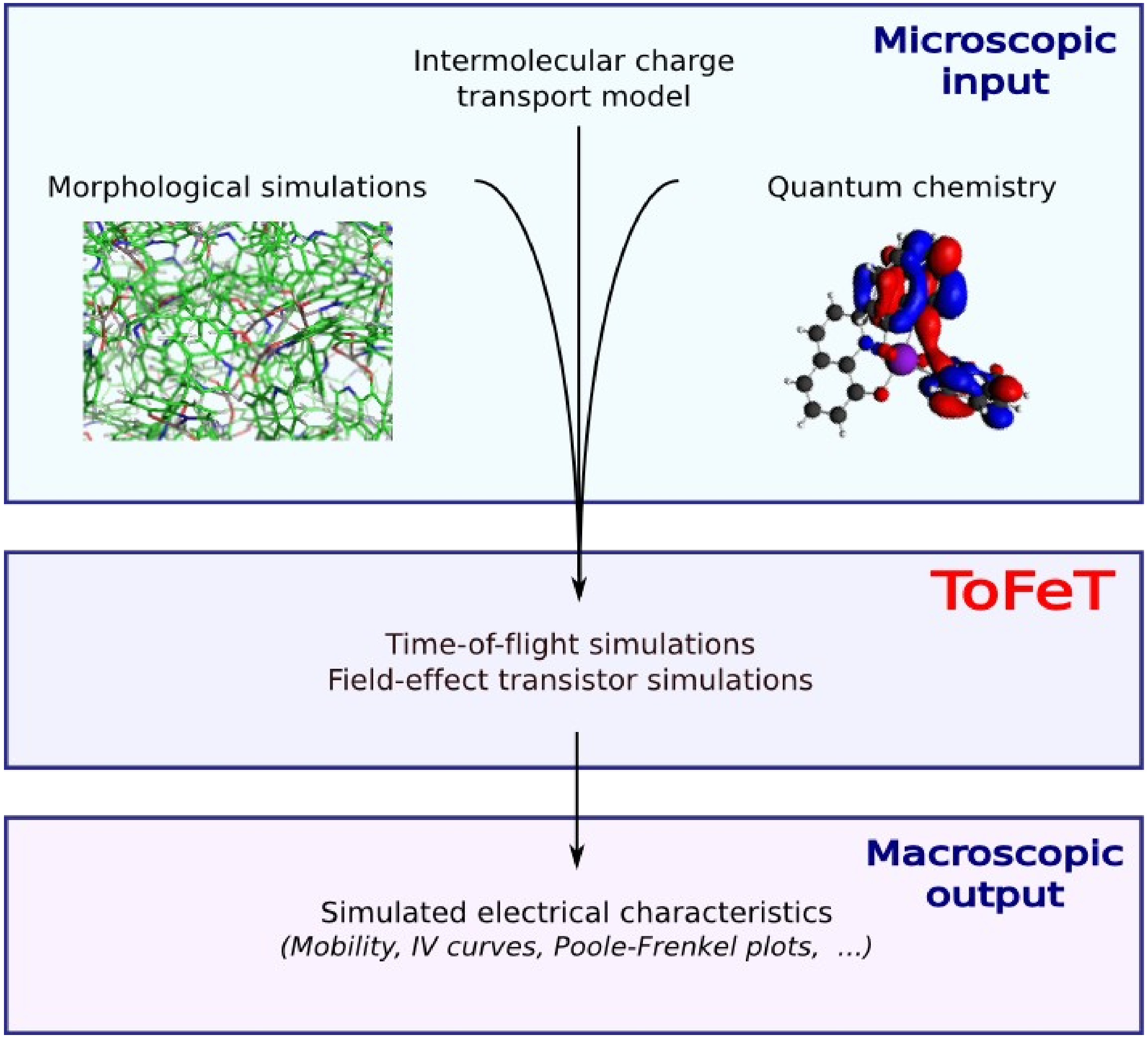
ToFeT: modelling organic electronic films



Microscopic input

Intermolecular charge transport model

Morphological simulations

Quantum chemistry

ToFeT

Time-of-flight simulations
Field-effect transistor simulations

Macroscopic output

Simulated electrical characteristics
(Mobility, IV curves, Poole-Frenkel plots, ...)

Relating the microscopic and macroscopic properties of organic electronic films.

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- Fully documented
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