Conference program, keynote speakers presentations and abstracts
Symposia

MC36: Theory: Density functional theory and beyond: Theory and applications

Monday 25th 11:30 - 12:30 – Room Belladonne

12:00-12:30 Charge transfer in organic and hybrid organic/inorganic systems from first principles
Patrick Rinke, Fritz Haber Institute of the Max Planck Society

Tuesday 26th 11:30 - 12:30 – “Optical Properties and Charge Transfer” - Room Pelletier

11:30-12:00 Optical properties of MoS2. Excitons beyond the bandgap
Alejandro Molina-Sanchez, University of Luxembourg

12:00-12:15 Interaction of tetrakis-Schiff base compounds with carbon nanostructures from DFT: implications for charge transfer.
Sergey Pyrlin, University of Minho

12:15-12:30 Towards a first-principles determination of effective Coulomb interactions in correlated electron materials: Role of intershell interactions
Priyanka Seth, Centre de Physique Théorique

Thursday 28th 11:30 - 12:30 – “Time-Dependent Density Functional Theory” - Room Pelletier

11:30-12:00 Electron energy loss and inelastic x-ray scattering cross sections from time-dependent density-functional perturbation theory
Iurii Timrov, Scuola Internazionale Superiore di Studi Avanzati / International School for Advanced Studies

12:00-12:15 Time-Dependent Density Functional Theory for Quantum Electrodynamics
Walter Tarantino, Laboratoire des Solides Irradiés

12:15-12:30 How to calculate Dynamical Structure Factors? From analysis to new methods
Igor Reshetnyak, Laboratoire des Solides Irradiés, European Theoretical Spectroscopy Facility

Thursday 28th 14:00 - 16:30 – Room Pelletier

14:00-14:30 The phonon-limited resistivity of graphene: electron-phonon interactions, screening and Boltzmann transport equation.
Thibault Sohier, Institut de minéralogie, de physique des matériaux et de cosmochimie

14:30-14:50 First-principles calculations of electron-phonon coupling in semiconductors
Jelena Sjakste, Laboratoire des Solides Irradiés, Ecole Polytechnique, CEA-DSM-IRAMIS CNRS
Interaction of tetrakis-Schiff base compounds with carbon nanostructures from DFT: implications for charge transfer.

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3. Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 - Tarragona, Spain;
4. Polymaterials AG. Innovapark 20, 87600 Kaufbeuren, Germany.
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Development of polymer composites by addition of nano-sized inclusions to matrix attracts increasing attention in the last decades as a potential way to prepare functional materials, the properties of which could be fine-tuned by varying the nanoadditives' concentration and alignment inside polymer. Carbon nanotubes (CNTs) and graphene nanoribbons (GNRs) are widely used as highly promising additives when high mechanical strength and good electrical conductivity are desired \cite{1}. However their poor interaction with surrounding matrix and tendency to form agglomerates lead to decline of material properties' improvement with increasing concentration \cite{2}. To tackle this problem surface functionalization is applied. However, as chemical bonding interrupts continuous sp2-bonded outer layer, the electrical properties could be severely damaged by grafting of functional groups. For this reason, there is a high demand for non-bonding functional molecules.

This work is focused on the interaction between CNT/GNR and tetrakis-Schiff base compounds. As it was shown previously \cite{3}, the later can form continuous networks of interconnected micrometer sized rings and rods with rim thickness of a few nanometers both on the surface and in the bulk of polymer. It was also noticed, that CNTs could be incorporated into these molecular networks and aligned along the rings and rods. Here we report the investigation of the interaction between tetrakis-Schiff bases and the surface of carbon nanotubes and graphene nanoribbons by means of density functional theory and molecular dynamics and its influence on the composite electrical properties studied by meso-scale Monte Carlo modeling.

Using the ONETEP \cite{4} and SIESTA \cite{5} density functional packages the relaxed structures of molecular complexes, consisting of CNT/GNR fragment and tetrakis-Schiff base molecule, were obtained both with and without van der Waals correction and the orientation dependant interaction energy were studied. A special attention is devoted to the frontier orbitals of the molecular complexes. It is shown, that HOMO and LUMO orbitals of the neighboring molecules and CNT/GNR surface level can overlap in the proximity of frontier orbitals of CNT/GNR thus facilitating charge transfer. For single base tetrakis-Schiff molecules with flat geometry a ballistic conduction channel appears for stacked molecular wire. For wedge-like double base molecules, forming the mentioned above ring-rod networks, with smaller overlap of frontier
orbitals and more complex mutual arrangement, the electron hopping model is proposed to investigate the effect of this peculiar interaction on the entire composite electric properties.

Final impact of CNT/GNR incorporation into self-assembled rings-and-rods molecular networks on the percolation threshold and conductivity of polymer composite is assessed by evaluation of resistivity of a model sample with molecular network, simulated with Monte Carlo method using the experimental data on rings distribution, sizes and connectivity. The resistivity of CNTs uniformly distributed, agglomerated and arranged in ring-rod network is compared.

Acknowledgments: The work was supported by European Community's Seventh Framework Programm through the Marie Curie Initial Training Network "CONTACT" for the tailored supply-chain development of CNT-filled composites with improved mechanical and electrical properties (FP7-PEOPLE-ITN-2008-238363) http://www.contactproject.eu/ and Portuguese Foundation for Science and Technology (FCT) through the PhD grant SFRH/BD/88995/2012. The Center of Physics of University of Minho research is sponsored by FEDER funds through COMPETE- Programa Operacional Factores de Competitividade and by national funds through FCT-Fundação para a Ciência e a Tecnologia, under the project PEst-C-FIS/UI607/2011-2012.

Self-assembling tetrakis-Schiff base compounds for CNT reinforced composites: combined MD, DFT & charge transfer study

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The research aim of ITN “CONTACT” is the tailored industrial supply-chain development of CNT-filled polymer composites with improved mechanical and electrical properties
Outline:

1. Introduction to CNT composites’ problems:
   - Why do we bother?
   - Why conventional way fails?
   - Any other way?

2. Computer study of self-assembly in double base compounds:
   - DFT&MD study of a single molecule and dimer
   - MD study of molecular ring self-assembly

3. Charge transfer properties of Schiff-base compounds
   - Single molecule electronic structure
   - Electron transfer in single tetkaris-Schiff base molecular system
   - Double tetrakis-Schiff base systems [work in progress]

This project has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363
Introduction to CNT composites’ problems: fantastic possibilities


Young modulus & Tensile strength increase $\sim 10$ by adding 1 vol% 
Conductivity increase $\sim 16$ orders of magnitude
Percolation threshold $\sim 0.003$ wt%

* Photographs from www.baytubes.com

This project has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363
Introduction to CNT composites’ problems: so why do we bother?

Anna Y. Matveeva, Ferrie W.J. van Hattum
I3N - Institute for Nanostructures, Nanomodelling and Nanofabrication, Portugal; www.i3n.org

* Photographs from www.baytubes.com

More – is not better!

Tensile tests (CNF/Epoxy) – experimental observation

Young modulus [Gpa]

-1% 0% 1% 2% 3%

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Introduction to CNT composites’ problems: so why do we bother?

What happened to my nanotubes???
- I’ve made a composite with 2 w.% of nanotubes!

- Indeed… and looks like all of them are here.

* Micro photograph from www.baytubes.com
Agglomerate size was determined from microscopy analysis of PC samples containing 3 vol. % of 1,5 um long CNTs.

<table>
<thead>
<tr>
<th>Code</th>
<th>average agglomerate radius $x_c$, um</th>
<th>agglomerate radius dispersion $w$, um</th>
<th>Volume resistivity ($\rho_v$) average</th>
<th>stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>0.28</td>
<td>1.55</td>
<td>78,908</td>
<td>3,965</td>
</tr>
<tr>
<td>F2</td>
<td>0.40</td>
<td>1.47</td>
<td>6171,026</td>
<td>2205,548</td>
</tr>
<tr>
<td>F3</td>
<td>0.41</td>
<td>0.85</td>
<td>27,934</td>
<td>2,025</td>
</tr>
<tr>
<td>F4</td>
<td>0.10</td>
<td>0.66</td>
<td>46,451</td>
<td>6,973</td>
</tr>
<tr>
<td>F5</td>
<td>0.14</td>
<td>0.53</td>
<td>156,873</td>
<td>28,616</td>
</tr>
<tr>
<td>F6</td>
<td>0.10</td>
<td>0.76</td>
<td>23,274</td>
<td>4,244</td>
</tr>
</tbody>
</table>

Series of samples with close agglomerate parameters can exhibit 2 orders of magnitude difference in resistivity.
Introduction to CNT composites’ problems: Why conventional way fails?

Resistor network model:

\[
\begin{align*}
\sum_i I_{ij} &= 0 \\
I_{ij} &= \frac{V_i - V_j}{R_{ij}} \\
V_i &= V_{ij} \sum_{j=2}^{n+2} a_{ij} = \sum_{j=2}^{n+2} a_{ij}V_j + a_{i1}V_1 + a_{i0}V_0 \\
&\rightarrow (I - A)V = B
\end{align*}
\]

Conclusion: the 2 order of magnitude difference cannot be attributed solely to agglomerate size - should be attributed to different degree of CNT alignment.
Introduction to CNT composites’ problems: 

*Any other way?*

Self-assembling molecular networks:


Nanorings and rods interconnected by self-assembly mimicking an artificial network of neurons.

Escárcega-Bobadilla MV¹, Zelada-Guillén GA, Pyrlin SV, et al.
Introduction to CNT composites’ problems: Any other way?

Self-assembling molecular networks: Monte Carlo study

Parameters:

Diameter 5.5+/−2.0 μm;
Rim 0.11+/−0.01 μm;
Rods per ring 2.8+/−0.7
CNT aspect ratio 65

Variation of volume resistivity (in a.u.) vs. average volume per ring (μm³/ring)

Percolation threshold:
- 2D down to ~0.06 surf. % (vs ~0.1 theory);
- 3D down to ~10⁻⁵ vol. % (vs ~1.0 theory);
Computer study of self-assembly in double base compounds:

DFT study of single tetrakis-Schiff molecule

• ONETEP: http://www2.tcm.phy.cam.ac.uk/onetep/
• SIESTA: http://departments.icmab.es/leem/siesta/
• NWChem: http://www.nwchem-sw.org/
• LAMMPS: http://lammps.sandia.gov/

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Computer study of self-assembly in double base compounds:

DFT & MD study of tetrakis-Schiff molecule dimer

<table>
<thead>
<tr>
<th>Bimolecular configuration</th>
<th>van der Waals binding energy (kcal/mol)</th>
<th>Coulomb binding energy (kcal/mol)</th>
<th>Total binding energy (absolute values, kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Back-to-back</td>
<td>~-40</td>
<td>+6 to +7</td>
<td>&gt; 30</td>
</tr>
<tr>
<td>b) Face-to-face</td>
<td>~-20</td>
<td>-6 to -7</td>
<td>~ 30</td>
</tr>
<tr>
<td>c) Stacked</td>
<td>~-30</td>
<td>-4 to 0</td>
<td>~ 30</td>
</tr>
<tr>
<td>d) Side contact</td>
<td>~ 20</td>
<td>~ -7 to 0</td>
<td>~ 15 to 30</td>
</tr>
</tbody>
</table>
MD study of tetrakis-Schiff molecular rings:

DREIDING force-field + DFT derived charges

Single and multi-molecular thick strings collapse into ring-like structures show no structural changes over microsecond simulation times
Electron transfer in single tetkaris-Schiff base molecular system

Flexible wedge-like structure:
- consists of 2 symmetric bases;
- provides stability in multi-molecular systems;
- Is a hell to optimize!

Single base compound:
- easier to optimize;
- features the basic phenomenon: cation-pi interaction;
This project has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

B3LYP, 6-31++G** for energy calculation
vdW-DF + optimized Becke 88* for geometry

Electron transfer in single tetkaris-Schiff base molecular system

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Electron transfer in single tetkaris-Schiff base molecular system

Expectation
Electron transfer in single tetkaris-Schiff base molecular system

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Expectation

Reality
Electron transfer in single tetkaris-Schiff base molecular system

\[ \lambda = (E_0^- - E_0^0) + (E_{-1}^0 - E_{-1}) \]

\[ V = \frac{J - S_{ij}(E_{ii} + E_{jj})/2}{1 - S_{ij}^2} \]

\[ K = \frac{|V|^2}{\hbar} \left( \frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left( \frac{\lambda}{4k_B T} \right) \]

\[ D = \frac{1}{2n} \sum_i r_i^2 K_i P_i \]

\[ \mu = \frac{eD}{k_B T} \]

146,4 meV

152,3 meV

2,5 \times 10^{14} \text{ s}^{-1}

2,33 \times 10^{-2} \text{ cm}^2/\text{s}

0,9 \text{ cm}^2/\text{Vs}


This project has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363
Work in progress:

• Constrained DFT study of charge transfer in double-base compounds;
Work in progress:

- Constrained DFT study of charge transfer in double-base compounds;
- MC study of charge transport in CNT-tetrakis-Schiff base compounds;
Acknowledgements:

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THANK YOU!