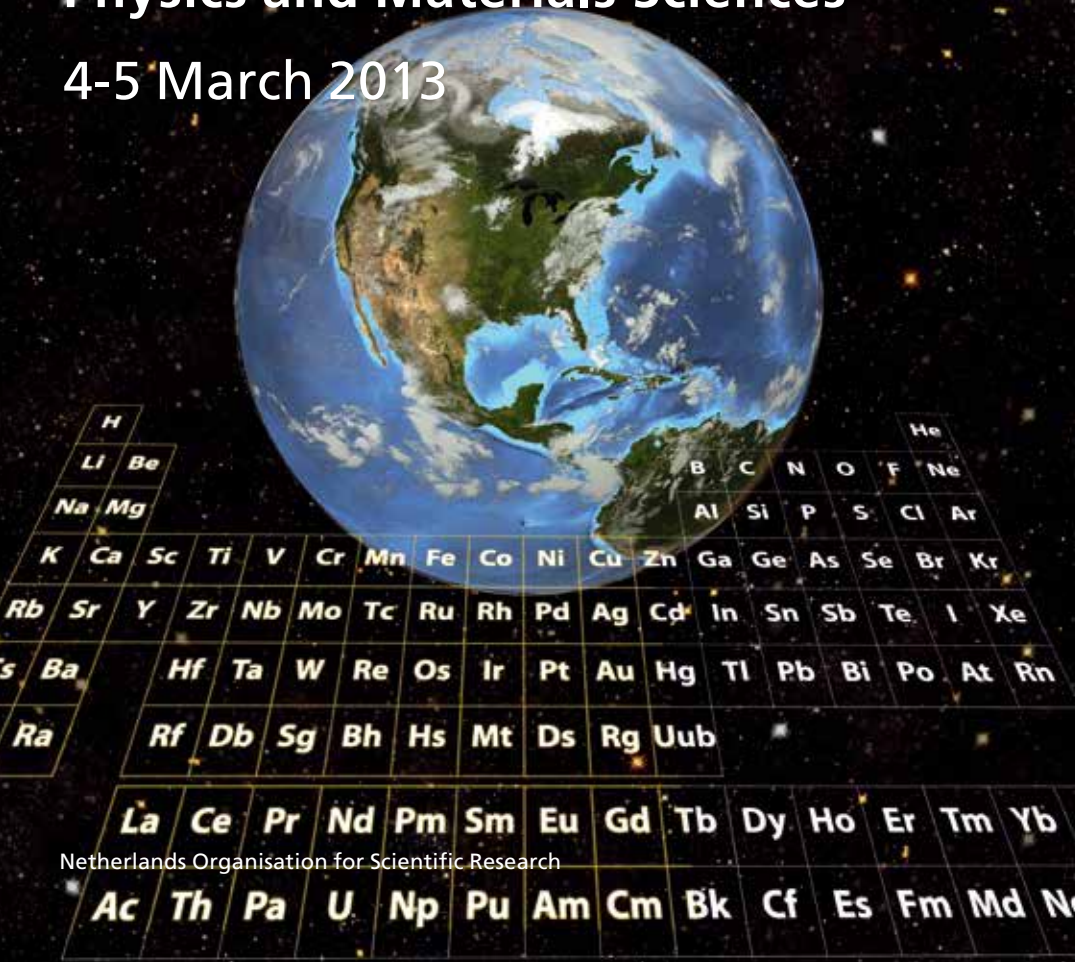
NWO CW Study group meeting

Chemistry in Relation to Physics and Materials Sciences

4-5 March 2013



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phase. Interestingly, we find that in our simulations intra and inter column jumps are highly correlated and caused by the collective movement of particles in and between pairs of column.

Phonon dynamics in DNA:determing the base-pair force constant

Author: **Lambert van Eijck**
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The biological functioning of DNA often involves mechanical operations on (parts of) the polymer and therefore depends, amongst others, on the mechanical properties of DNA. The genetic code can be accessed by opening of the base pairs and if DNA is not operated on from the polymer ends, then base pair opening is co-existing with bubble formation: a series of consecutive base pairs that are opened. The statistical abundance of bubbles in a DNA polymer is related to its mechanical properties in a model proposed by Peyrard and colleagues [1].

By wet-spinning we are able to make large quantities of aligned DNA fibers required for neutron scattering experiments. Inelastic neutron scattering allows us to measure in the acoustic phonons in B-DNA, a direct measure of the base pair force constant [2]. The reported values on this constant in literature vary by more than 2 orders of magnitude and we reconcile these variations with our findings using an atomistic model of DNA. The dependence of the phonon dynamics on humidity and different forms of DNA is investigated.

[1] Peyrard, Nature Physics 2, p 13 (2006)
[2] L. van Eijck et. al, Phys Rev. Lett 107, 088102 (2011)

Coarse-grained simulations of linear and star polymer melts

Author: **Li Liu**
Co-authors: *J.T. Padding, W.K. Den Otter and W.J. Briels*
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A computational study on entangled polyethylene melts with different topologies is carried out by the TWENTANGLEMENT simulation technique. In our simulations, groups of 20 carbons are coarsegrained into one ‘blob’. Because of the high coarse-graining level,the effective potential between blobs becomes so soft that blob-blob bonds can cross each other. In order to prevent these unrealistic crossings, uncrossability constraints are applied. After successful simulations of linear polymers, we extended the program to

handle branched polymers. We present dynamical and rheological properties of 3-arm star polyethylene melts, and discuss the similarities and differences with linear polymers of two and three star arm lengths. We also analyze the dynamics in terms of the Rouse modes for stars.

Session 5 –Spectroscopy: Photodynamics

Active and Passive Control of Zinc Phthalocyanine Photodynamics

Author: **Annemarie Huijser**
Co-authors: *Divya Sharma, Gerwin Steen and Jennifer Herek*
University of Twente

In this presentation we will focus on the ultrafast photodynamics of the photosensitizer zinc phthalocyanine (ZnPc) and manipulation thereof. Two approaches are followed: active control via pulse shaping and passive control via strategic manipulation in the periphery of the molecular structure. The objective of both of these control experiments is the same: to enhance the yield of the functional pathway and to minimize loss channels. The aim of the active control experiments is to increase the intersystem crossing yield in ZnPc, which is important for application in photodynamic therapy (PDT). Pulse shaping allowed an improvement in triplet to singlet ratio of 15% as compared to a transform-limited pulse. This effect is ascribed to a control mechanism that utilizes multiphoton pathways to higher-lying states from where intersystem crossing is more likely to occur. The passive control experiments are performed on ZnPc derivatives deposited onto TiO2, serving as a model system of a dye-sensitized solar cell (DSSC). Modification of the anchoring ligand of the molecular structure resulted in an increased rate for electron injection into TiO2 and slower back electron transfer, improving the DSSC efficiency.

Excited state dynamics of Photoactive Yellow Protein chromophores elucidated by high-resolution spectroscopy and ab initio calculations

Author: **Eric Tan**
Co-authors: *Saeed Amirjalayer, Bert H. Bakker and Wybren J. Buma*
University of Amsterdam

We report on experimental high-resolution spectroscopic studies in combination with advanced theoretical calculations that focus on the excited-state dynamics of various forms of the chromophore of the Photoactive Yellow Protein (PYP), and the dependence of these dynamics on conformational and isosteric structure, as well as the biological environment. Three-colour nanosecond multiphoton ionization pump-probe