

CPP 11: New Instruments and Methods

Time: Tuesday 9:30–13:00

Location: C 243

Topical Talk

CPP 11.1 Tue 9:30 C 243

Employing natural search strategies for complex optimization problems — CHRISTOPH SCHIFFMANN and DANIEL SEBASTIANI — Freie Universität Berlin

The Artificial Bee Colony algorithm¹ is a stochastic optimization scheme that mimics the foraging behavior of honey bees. As one of the most recently developed “nature-inspired” algorithms, this approach has turned out to perform very efficiently in global optimization problems from engineering and computer science.

We apply the Artificial Bee Colony algorithm to optimization problems² in chemical physics, specifically within ab-initio electronic structure theory. This field is a case in point for highly corrugated potential surfaces which render deterministic approaches unfeasible.

¹ Karaboga, D. & Basturk, B. *J. Glob. Optim.*, **2007**, 39(3), 459–471.

² Schiffmann, C. & Sebastiani, D. *J. Chem. Theory Comput.*, **2011**, 7(5), 1307–1315.

CPP 11.2 Tue 10:00 C 243

Excitation Energy Transfer and Optical Properties of Supramolecular Complexes: A Mixed Quantum Classical Methodology — JÖRG MEGOW¹, ALEXANDER KULESZA², BEATE RÖDER¹, ROLAND MITRIC², and VOLKHARD MAY¹ — ¹Institut für Physik, Humboldt-Universität zu Berlin, Germany — ²Institut für Physik, Freie Universität Berlin, Germany

Excitation energy transfer and optical properties of large chromophore complexes are studied using a mixed quantum classical methodology. The chromophore complex is formed by a butanediamine dendrimer to which sixteen pheophorbide-a (Pheo) molecules are covalently linked (P16). While the nuclear coordinates are described classically by carrying out room-temperature MD-simulations the electronic excitations are treated quantum mechanically by solving the time-dependent Schrödinger equation. The energy gap fluctuation due to intramolecular vibration was calculated utilizing a harmonic approximation. The solute-solvent coupling is treated by Coulomb interaction.

Using the energy gap fluctuation, linear absorbance and pump-probe-spectra of P16 are calculated and compared to earlier results calculated for a single Pheo [1] and P4 [2,3]. The effect of the excitonic coupling between the chromophores in P16 was analyzed in comparison with the results for a single Pheo and P4.

[1] J. Megow et al., *Chem. Phys.* **377**, 10 (2010)

[2] J. Megow et al., *ChemPhysChem* **12**, 645 (2011)

[3] J. Megow et al., *Chem. Phys. Lett.* (in press)

CPP 11.3 Tue 10:15 C 243

A numerical approach to macroscopic nuclear spin-lattice relaxation by paramagnetic impurities — SIMON QUITTEK, MICHAEL DITTER, and FRANZ FUJARA — Institut für Festkörperphysik, TU Darmstadt

The influence of paramagnetic impurities on the nuclear spin-lattice relaxation rate has been known for about fifty years. Good heat contact between both systems favors a relaxation path from the nuclei via the impurities into the lattice, which considerably speeds up the bulk relaxation.

Whereas microscopic theory is well investigated, we lack a detailed understanding of the macroscopic processes. Recent field-cycling NMR data reveal a field dependence of the relaxation rate that is not comprised by conventional methods.

To shed some light onto this up-to-date problem, a computer simulation has been performed. The combined relaxation-diffusion equation is solved *ab initio* in a deterministic numeric scheme, which discretizes the considered space. An alternative approach maps the diffusion component onto random walkers, which in turn carry magnetization that is gradually lost when approaching an impurity.

The calculations yield relaxation behaviour that is in good agreement with experimental data. Impurity distributions and magnetic fields are reflected in the field dependent relaxation rates.

CPP 11.4 Tue 10:30 C 243

Temperature modulated optical refractometry: a novel access to structural changes in isotropic media coupling to the optical refractive index — ULRICH MÜLLER¹, MARTINE PHILIPP², ROLAND SANCTUARY¹, PETER MÜLLER-BUSCHBAUM², and

JAN-KRISTIAN KRÜGER¹ — ¹Université du Luxembourg, Laboratoire de physique des matériaux avancés, 162a av. de la faïencerie, Luxembourg, Luxembourg — ²TU München, LS Funktionelle Materialien, Garching, Germany

Temperature modulated optical refractometry (TMOR) is a novel technique that provides access to the dynamic thermo-optic coefficient $\phi^*(\omega) = \frac{1}{n} \frac{dn}{dT}(\omega)$. Similar to temperature modulated calorimetry small sinusoidal temperature perturbations are applied to the sample and their effect on its refractive index n is measured. By applying linear response theory the usually complex susceptibility $\phi^*(\omega)$ is obtained. Simultaneously, the mean refractive index yields information about kinetically induced structural changes. Using the Lorenz-Lorentz equation to relate the refractive index to the mass density the complex coefficient of thermal expansion $\alpha^*(\omega)$ can be calculated out of n and $\phi^*(\omega)$. This novel technique is especially suited for the investigation of (isothermal) structure-changing processes like polymerization, solvent evaporation, and isostructural phase transitions (e.g. glass transitions or volume phase transitions), where it allows for an easy discrimination of kinetic and dynamic contributions. Investigations of the chemically induced glass transition in an epoxy and of the volume phase transition in PNIPAM/water are presented as applications.

CPP 11.5 Tue 10:45 C 243

Infrared Transition Moment Orientational Analysis on semi-crystalline polyethylene films — WILHELM KOSSACK¹, PERIKLIS PAPADOPOULOS², MATTHEW PARKINSON³, FLORAN PRADES³, and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany — ²Max Planck Institute for Polymer Research, Postfach 3148, 55021 Mainz, Germany — ³Borealis Polyolefine GmbH, St.-Peter-Strasse 25, 4021 Linz, Austria

The recently developed method of Infrared-Transition-Moment-Orientational-Analysis (IR-TMOA) is based on concurrent measurements of the transmission in dependence on polarisation of the IR light and on the inclination of the sample with respect to the optical axis. This enables one to determine for the different molecular moieties of the studied material the full order parameter tensor and its orientation with respect to the sample coordinate system. The analysed films, made by a blown film process, show only low ordered crystalline regions (order parameters <0.3) and an even less ordered amorphous matrix (Kossack, et al., doi:10.1016/j.polymer.2011.10.051). The method provides a quantitative insight into the correlation of production parameters and microscopic structure playing a key role to improve the properties of polyolefin films.

CPP 11.6 Tue 11:00 C 243

Characterization of morphology and orientation of uni-axially oriented cast films with confocal and polarized μ -Raman Imaging-Spectroscopy — KRISZTINA VINCZE-MINYA, TOBIAS KEPLINGER, and SABINE HILD — Institute of Polymer Science, Johannes Kepler University, Altenbergerstr. 69, 4040 Linz, Austria

The morphology of a semi-crystalline polymer has a great bearing on its mechanical strength. The ratio of crystalline and amorphous phases and molecular orientation in these phases are essential to optimize the physical properties. Confocal μ -Raman microscopy is a useful characterization technique to characterize the orientation not only of the crystalline but also of the amorphous phase. With confocal μ -Raman Imaging it is possible to calculate not only an average crystallinity, but also to determine the local crystallinity. The main focus is to calculate the crystallinity degree and to characterize the orientation of the uni-axially oriented PP cast films. The ratio of the peaks at 841 and 809 cm⁻¹ is sensitive to the molecular anisotropy and the crystallinity values were calculated by the Nielsen method[1]. The ratios $I(809)/I(841)$ and $I(973)/I(998)$ are used for the characterization of orientation heterogeneity (I = intensity of a peak)[2]. Based on these results the orientation and crystallinity of shear crystallized samples are investigated. [1]Nielsen A.S., Batchelder D.N., Pyrz R., 2002, *Polymer*, **43**(9), 2671–2676 [2]J. Martin, S. Margueron, M. Fontana, M. Cochez, P. Bourson, 2009, *Polymer Engineering & Science*, **50**(1), 138–143

15 min break

CPP 11.7 Tue 11:30 C 243

Twin-Focus Photothermal Correlation Spectroscopy — ●MARKUS SELMKE, MARCO BRAUN, ROMY SCHACHOFF, and FRANK CICHOS — Universität Leipzig, Exp. Physik I, molecular nanophotonics

The use of metal nano-particles for probing dynamics and reactions in biology and soft-matter physics has been on the rise due to their superior stability as compared to molecular fluorophores. The successful method of fluorescence correlation spectroscopy (FCS), which quantifies in its simplest form locally the diffusion and mobilities, has found its counterpart for these non-fluorescent but absorbing nano-tracers in PhoCS, photothermal correlation spectroscopy. The signal used in this method for the detection is related to the plasmonic heating of the particles: The power absorbed from a resonant laser (532nm) generates a temperature profile around the particle which in turn causes a refractive index profile which is probed by a second off-resonance laser, typically by means of a lock-in technique. While the lensing action provides a twin-focus split detection-volume in which two non-overlapping regions may be addressed and analyzed individually or in combination it is also clear that the absorption infers momentum to the diffusing particles which may be addressed and studied by the advection-diffusion equation and its effect on various (cross-)correlation functions. These features allow for the sensitive determination of minute flow velocities, either self-induced by radiation pressure or via external forces, and the study of heterogeneous dynamics on the length scale of the split-focus separation (about 500nm).

CPP 11.8 Tue 11:45 C 243

Organic reactions at ionic liquid surfaces studied by in-situ XPS — ●INGA NIEDERMAIER¹, CLAUDIA KOLBECK¹, NICOLA TACCARDI², PETER SCHULZ², PETER WASSERSCHIED², HANS-PETER STEINRÜCK¹, and FLORIAN MAIER¹ — ¹Lehrstuhl für Physikalische Chemie II, Egerlandstr. 3, 91058 Erlangen — ²Lehrstuhl für Chemische Reaktionstechnik, Egerlandstr. 3, 91058 Erlangen

Due to their low vapour pressure, ionic liquids - organic salts with a melting point below 100 °C - can be investigated by surface science techniques under UHV conditions. In particular, angle-resolved X-ray photoelectron spectroscopy (ARXPS) has been proven to be an effective tool for studying molecular enrichment and orientation effects even for the topmost surface layers of the ionic liquid. Here, we demonstrate that ARXPS also allows accessing classical organic chemical reactions normally carried out in common solvents, by employing reactive centres covalently fixed to cations or anions of ILs. This novel concept is successfully carried out for a nucleophilic substitution where a tertiary amine attached to an imidazolium cation is alkylated by the chloroalkyl moiety of the anion. In course of the reaction, covalently bound chlorine (neutral) is converted to chloride (negatively charged) and amine (neutral) to ammonium (positively charged). These changes are reflected by characteristic shifts in the N 1s and Cl 2p ARXP spectra. In this respect, in-situ ARXPS represents a novel tool to analyse reaction pathways at liquid surfaces on a molecular level. - Supported by the DFG through SPP 1191 and by the Cluster of Excellence - Engineering of Advanced Materials.

CPP 11.9 Tue 12:00 C 243

Piezoelectric PVDF as an acoustically calibrated transducer — ●MARCEL KAPPEL, GUNNAR GIDION, and REIMUND GERHARD — Universität Potsdam, Institut für Physik und Astronomie, Potsdam

The application of piezoelectric polyvinylidene fluoride (PVDF) as a calibrated acoustical sensor is tested and characterized with different methods. Characteristic parameters, such as the static pressure and the amplitude of the dynamical force on the PVDF film, as well as the sensor long term stability, are varied in order to evaluate the effectivity and durability of the electro-mechanical conversion represented by the piezoelectric coefficient d_{33} . Also the frequency response of the piezopolymer as sensor and actuator was investigated. Using thin film sensors made from PVDF, we describe measurements made on a conceptional piano model and on a real piano manufactured by Bechstein. The PVDF probes were mounted between the resonance board and the sound bridge, in combination with a condenser microphone for airborne sound. Beside both recording techniques were directly compared, the temporal distribution of the vibrational energy within the measured setup could be deduced.

CPP 11.10 Tue 12:15 C 243

Soft colloidal probe AFM for quantifying mechanoresponsive

brushes — ●JOHANN ERATH¹, JOHANNA BÜNSOW², WILHELM T. S. HUCK^{2,3}, and ANDREAS FERY¹ — ¹Physical Chemistry II, University Bayreuth, Universitätsstraße 30, 95440, Bayreuth, Germany — ²Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB21EW, UK — ³Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

The aim of this contribution is to introduce a novel concept for self-reporting force sensors based on mechano-responsive polyelectrolyte brushes, which translate deformation and tension directly into changes of fluorescence intensity[1]. Force sensing experiments were performed with a combination of an atomic force microscope (AFM) with a confocal laser scanning microscope (CLSM), using the soft colloidal probe (SCP) technique. On the basis of the JKR theory, we developed a quantitative understanding of the force distribution underneath the PDMS bead, which shows that the sensor does response to compression and tension. We find an excellent pressure sensitivity in the order of 1 kPa and a lateral resolution better than 1 micron. Beside the basic concept of the technique we will show perspectives for mapping pressure fields.

[1] Bünsow, J.; Erath, J.; Biesheuvel, M.; Fery, A.; Huck, W. T. S., *Angewandte Chem. Int. Ed.*, 50, (2011) 9629-9632 Highlighted by *Nature Materials* 2011, 10, p. 724

CPP 11.11 Tue 12:30 C 243

Application of novel thermal cantilever in the field of polymer science — ●THOMAS FISCHINGER, MARTIN LAHER, GÜNTHER GRATZL, and SABINE HILD — Department of Polymer Sciences, Johannes Kepler University, Linz, Austria

Thermal analysis methods are generally used to provide important and reliable data on polymeric materials. However, up to now mainly bulk properties of polymers have been detected. Their fields of operation reach a limit for applications such as investigation of thin films, immiscible polymer blends, boundary effects etc. Therefore, a method is proposed for nano-thermal characterization of polymers using scanning probe microscopy in combination with heatable cantilever probes. This method is based on an appropriate temperature calibration, which provides a reliable correlation between applied voltage and the temperature at the tip. Since it has been shown that the presented technique is substantially more susceptible to environmental changes, such as layer thickness, substrate material etc. than comparable macroscopic approaches, parameters that might influence the performance have been evaluated. To verify the validity and show the possibilities of this method, local thermal analysis measurements were performed on different polymer samples. The glass transition- and melting temperature obtained by our approach agrees well with the value measured using conventional bulk methods.

CPP 11.12 Tue 12:45 C 243

Bimetallic cantilever microcalorimetry with high energy and time resolution — ●FLORIAN M. SPIRKL, RICHARD SCHRÖTER, FRIEDRICH ESCH, and ULI HEIZ — TU München, Lehrstuhl f. Physikalische Chemie

Temperature induced bending of bimetallic cantilevers has been established in recent years as sensor for microcalorimetry, offering high energy resolution [1]. The position of the cantilever tip is read out using a laser and a position sensitive optical device (PSD). We present a differential read out setup that improves the time resolution from typical 100 ms [2] down to 1 ms, the response time of the cantilevers that is time-limiting.

The experimental setup consists of a reactive sample and an inert reference cantilever that are read out differentially using a high frequency deflection mirror. Both bend simultaneously due to environment changes, whereas the investigated process develops heat only on the sample cantilever. For calibration, both sample and reference cantilever can be heated by two laser diodes. This cantilever setup works under UHV conditions, and in reactive gas as well as in liquid environment. The sensitivity of the ambient cantilever setup can be estimated to be 150 nJ with 1 ms time resolution.

First experiments within a temperature controlled liquid flow cell will be presented, including measurements on thiol-gold bonding upon formation of self-assembled monolayers (SAM).

[1] J.R. Barnes *et. al.*, *Review of Scientific Instruments* **65**, 3793, (1994) [2] H.P. Lang *et. al.*, *Materials Today* **8**, 30 (2005)