CPP 15: Poster: New Instruments and Methods

Time: Tuesday 18:15–20:15 Location: Poster A

CPP 15.1 Tue 18:15 Poster A

Investigating microfluidics at interfaces with GISAXS — •Volker Körstgens[1], Kuhu Sarkar[1], Martin Trebbin[2], Matthias Schwartzkopf[3], Adeline Bufffet[3], Stephan V. Roth[3], Stephan Förster[2], and Peter Müller-Buschbaum[1] — [1]TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany — [2]Universität Bayreuth, Physikalische Chemie I, 95447 Bayreuth, Germany — [3]HASYLAB at DESY, 22603 Hamburg, Germany

X-rays are a powerful probe for the investigation of flow and processes in microfluidic systems. In pioneering experiments it has been shown that with GISAXS (grazing incidence small angle x-ray scattering), using a specially designed microfluidic cell, surface sensitive investigations are also possible [1]. With the highly brillant x-ray beam available at the beamline MiNaXS of the PETRA III synchrotron source a time resolved as well as a position resolved GISAXS investigation of structural changes at the surface in contact with the flowing liquid becomes possible. The microfluidic cell design offers versatile options including mixing experiments and chemical reactions. Swelling processes, the attachment of particles and also the detachment of unwanted detrimental films can be investigated. The envisaged high time resolution will allow to follow the corresponding kinetics.

This work has been financially supported by the BMBF (grant number 05K10WOA).

[1] J.-F. Moulin et al., Rev. Sci. Instrum. 79, 015109 (2008).

CPP 15.2 Tue 18:15 Poster A

The small angle scattering beamline BW4 of HASYLAB: Recent developments and future perspectives — •Jan Perlich, Jan Rubeck, Stephan V. Roth, and Rainer Gehrke — HASYLAB-DESY, Notkestr. 85, D-22603 Hamburg (Germany)

The small angle scattering beamline BW4 of HASYLAB, Hamburg (Germany), is a dedicated materials science beamline. The main experimental techniques are transmission small angle X-ray scattering (SAXS) as well as grazing incidence small angle X-ray scattering (GISAXS) in reflection geometry. The implemented microfocus option at the BW4 instrument [1] enables experiments where lateral scanning of sample materials is feasible. After major refurbishments of the beamline in the recent years, the focus is on expanding the experimental capabilities by the access to an extended scattering q-range, e.g. GIWAXS [2], and the introduction of necessary sample environments for the structural characterization of novel material systems at specific physical conditions. In addition, in-situ sample observations are possible with a fast detector enabling the structural characterization of time-dependent processes. We present the novel experimental capabilities based on selected recent results [3]. Based on the outstanding performance of this beamline for 20 years, BW4 will remain unforgotten!

[1] Roth et al., Rev. Sci. Instrum. 77 (2006), 085106.
[2] Perlich et al., Rev. Sci. Instrum. 81 (2010), 105105.
[3] Perlich et al., Phys. Status Solidi RRL 3(4) (2009), 118.

CPP 15.3 Tue 18:15 Poster A

A novel Dilatometer to investigate the influence of pressure, cooling rate and shear rate on the specific Volume of polymers. — •Sibylle Jilg, Reinhard Forstner, and Wolfgang Stadlbauer — Transfercenter für Kunststofftechnik GmbH, Franz-Fritsch-Straße 11, 4600 Wels, Austria

These novel pvT-Dilatometer (Pirouette-pvT-Apparatus) was designed to measure the specific volume of polymers under processing conditions as found in injection moulding. So it is possible to investigate the specific volume as a function of temperature (up to 300°C), pressure (up to 1000 bar), cooling rate (up to 100°C/s) and shear rate (up to 180 1/s). The Pirouette is a combination of a traditional piston-die dilatometer and a Couette rheometer. This dilatometer can be used in several operating modes. Isobaric heating, isobaric cooling and isothermal experiments are possible. In this investigation measurements were performed with isotactic Homo-Polypropylenes in the isobaric cooling mode to show the dependency of the transition temperature from pressure, cooling rate and shear flow. It can be found that increasing pressure shifts the transition temperature to higher temperatures and higher cooling rates shifts the transition temperature to lower values. Higher shear temperatures shift the transition temperature to higher temperatures and higher pressures enhance the effect of shear. The specific volume after cooling to room temperature is mainly depending on cooling rate.

CPP 15.4 Tue 18:15 Poster A

Characterization of AFM tips using graphite steps — •Friedrich Lüders, Ann-Kristin Löhmann, and Thomas Thurn-Albrecht — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Germany

To investigate the morphology and mechanical characteristics of soft polymer samples on the nanometer scale, Atomic Force Microscopy (AFM) in Intermittent Contact Mode (ICM) is a commonly used technique. The AFM image is always a convolution of the surface topography and the shape of the tip. The resolution of an image is therefore limited by the sharpness of the tip. Also in ICM the tip indents into the sample, into softer areas more than in harder regions. For a quantitative analysis of AFM images the exact shape of the tip must be known.

We present a simple method for characterization of an AFM tip by scanning the steps between different layers (0.355 nm high) on a graphite surface. These atomic steps provide a much higher aspect ratio than standard AFM tips (radius 5-10nm) and hence can be used for the tip characterization. The image of a graphite step contains information about the shape of the lowest few nanometers of the tip. The width of the imaged step can be used as a measure for the resolution.

To test the results of the calibration method, a sample of hexacontane on graphite was used. As expected the lamellar structure of the sample with a periodicity of 7.5 nm could be imaged with sharp tips while with the blunter tips imaging of the lamellae was impossible.

CPP 15.5 Tue 18:15 Poster A

Impurity Spectroscopy at its Ultimate Limit: Relation between Bulk Spectrum and the Distributions of Individual Parameters of (Nearly) All Dopant Molecules in Solids — Andrei V. Naumov[1], Aleksey A. Gorshelev[1], Yury G. Vainer[1], •Lothar Kador[2], and Jürgen Köhler[2] — [1]Molecular Spectroscopy Department, Institute for Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow reg., 142190, Russia — [2]University of Bayreuth, Institute of Physics and Bayreuther Institut für Makromolekülforschung (BIMF), 95440 Bayreuth, Germany

We recorded the fluorescence excitation spectra of a substantial fraction of all single chromophore molecules (hundreds of thousands and more) in solid bulk samples. The complete spectra and the spatial coordinates of all chromophores were stored for further analysis. In this way it is possible to study a bulk sample in a broad spectral region given by the inhomogeneous width of the electronic transition with ultimate sensitivity, combining excellent statistical accuracy and the capability of detecting rare events. From the raw data, the distributions of a number of parameters of the chromophore spectra were extracted, including the frequencies of the zero-phonon lines, their linewidths, and fluorescence count rates. Relationships between these distributions and the disorder of the matrix were established for the examples of two polycrystalline matrices of very different properties, *n*-hexadecane and *o*-dichlorobenzene, and the amorphous polymer polyisobutylene. Spatially inhomogeneous distributions of some parameters were found.

CPP 15.6 Tue 18:15 Poster A

Conceptual design for a new small angle X-ray scattering instrument at the Petra III extension — •Rainer Gehrke, Ulla Vainio, and Jan Perlich — Deutsches Elektronensynchrotron DESY, Notkestrasse 85, D-22603 Hamburg (Germany)

The storage ring DORIS III at DESY/Hamburg will stop operation at the end of 2012. A couple of experimental techniques which are presently not available at PETRA III have to be established at the new machine. Among these techniques are the various kinds of small angle X-ray scattering with moderately focused beams which are carried out at DORIS III beamlines A2, B1, and BW4 at present. In the frame of a PETRA III extension project a new versatile SAXS instrument is under planning which will allow performing SAXS in transmission and reflection geometry. It will feature a mini-undulator, a non-dispersive double crystal monochromator, horizontally and ver-

tically focusing mirrors, and a maximum sample to detector distance of about 20 meters. The planned setup will also offer to utilize anomalous scattering in all possible scattering geometries.

The details of the components of the beamline layout (source, optics, experimental hutch) are discussed and ray tracing calculations are presented which allow estimating the beam properties in terms of beamsize, photon flux, etc.

CPP 15.7 Tue 18:15 Poster A

A sample holder for soft x-ray absorption spectroscopy of liquids in transmssion mode — •Simon Schreck, Gianina Gavrila, Christian Weniger, and Philippe Wernet — Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin, Germany

Applying soft x-rays to liquids is challenging due to the incompatibility of the vacuum environment required for soft x-rays and the high vapor pressure of liquids. When recording soft x-ray absorption spectra in transmission mode, which is the most direct and efficient way, the strong attenuation of soft x-rays in matter calls for ultrathin samples.

Here we present a novel sample holder for soft x-ray absorption spectroscopy of liquids in transmission mode based on sample cells with x-ray transparent silicon nitride membranes. The sample holder allows for a reliable preparation of ultrathin liquid films with an adjustable thickness in the nm-μm range. This enables measurements of high quality x-ray absorption spectra of liquids in transmission mode, as will be shown for the example of liquid H2O, aqueous solutions of 3d-transition metal ions and alcohol-water mixtures. The fine structure of the x-ray absorption spectra is not affected by the sample thickness. No effects of the silicon nitride membranes were observed in the spectra. It is shown how an inhomogeneous thickness of the sample affects the spectra and how this can be avoided.

The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

CPP 15.8 Tue 18:15 Poster A

Combining UV-Vis and microGISAXS — •Roman Mannweiler[1], Matthias Schwartzkopf[1,2], Johannes F. H. Risch[1], Sebastian Bommel[1,3], Alke Meents[1], and Stephan V. Roth[1] — [1]Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, D-22607 Hamburg, Germany — [2]Universität Hamburg, Institut für Technische und Makromolekulare Chemie, Bundesstr. 45 20146 Hamburg, Germany — [3]Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

Due to the immense technical development going hand in hand with a growing need for raw materials especially for metals, we must consider that our resources are finite. Therefore there is a growing need for alternative materials, which can easily be produced and have tailored properties at the same time which is one of the tremendous advantages of nanocomposites. In detail, polymer-metal nanocomposites can be designed by using different types of nano-particles and coating-procedures, so that they deliver many possibilities for different applications, like optical wirings in processing units or photovoltaic devices. Here, we restrict ourselves to determining the optical properties of such a nanocomposite by using UV-Vis-Spectroscopy. We present two applications examples, namely sputter-deposited gradient samples as well colloidal layer systems, to relate nanostructural changes with spectroscopic features.

CPP 15.9 Tue 18:15 Poster A

Soft x-ray emission spectroscopy on liquid jets - probing valence structure of solvents and solutes — •Kristjan Kunnus[1], Martin Beye[1], Alexander Föhlisch[1], Christian Kalus[1], Kerstin Kalus[1], Wilson Quevedo[1], Simon Schreck[1], Edlira Suljoti[1], Christian Weniger[1], Philippe Wernet[1], Sebastian Grübel[2], Ivan Rajkovic[2], Simone Techert[2], Franz Hennies[3], and Brian Kennedy[3] — [1]Helmholtz-Zentrum Berlin, Berlin, Germany — [2]Max-Planck-Institut für Biophysikalische Chemie, Göttingen, Germany — [3]MAX-lab, Lund, Sweden

We have developed an experimental set up which combines an in vacuum liquid jet with a soft x-ray emission spectrometer to enable resonant inelastic soft x-ray scattering (RIXS) measurements from liquids. RIXS is a powerful technique which enables to probe occupied and unoccupied electronic states with elemental and chemical selectivity. Advantages of using a liquid jet are continuous replenishment of the sample and absence of membranes to separate the liquid from the vacuum. These properties make the setup suitable for complementary usage at synchrotrons and x-ray free electron laser facilities. As example, RIXS L-edge spectra of $K_3[Fe(CN)_6]$ and $CrCl_3$ aqueous solutions together with K-edge spectra of bulk water and alcohols are presented. These measurements were done at the BESSYII synchrotron radiation facility in Berlin, Germany.

CPP 15.10 Tue 18:15 Poster A

Space-resolved dynamic light scattering probing inhomogeneous dynamics in soft matter — •Sebastian Golde, Markus Franke, and Hans Joachim Schöpe — JoGu Universität Mainz, Institut für Physik, Staudinger Weg 7, 55099 Mainz, Germany

Dynamic light scattering (DLS) is the most powerful tool determining the dynamics in soft matter in a huge time interval of eleven decades. Using standard techniques the ensemble averaged dynamics can be determined in ergodic media. In nonergodic samples the time-averaged and the ensemble-averaged one differ. Special techniques have been developed (Interleaved sampling [1], Echo technique [2], multispeckle (MS) analysis [3]), measuring the intensity autocorrelation function (ICF) of many different coherent areas (speckles) simultaneously, in order to obtain ensemble averaged data. We here present a comparison of a new designed MS-DLS experiment with the Echo technique. In order to measure many speckles simultaneously we map the sample onto a fast CCD as a detector, which allows us to monitore the intensity of more than 500 speckles simultaneously and to connect each speckle with its origin scattering volume. Comparing the results from different method we obtain identical ensemble averaged results for colloidal hard sphere glasses. With the MS method we can achieve three decades shorter delay times than with the Echo method. Furthermore the MS setup allows us to measure time-resolved as well as space-resolved ICFs to probe differences in spatially separated subensembles. [1]Pr.Coll.Pol.Sci.100,121(1996) [2]Re.Sci.Inst. 75,2419(2004) [3]JCP 104,1758(1996)

CPP 15.11 Tue 18:15 Poster A

NMR spectroscopy in pulsed high magnetic fields — Benno Meier[1,2], •Jonas Kohlrautz[1], Jürgen Haase[1], Frederik Wolff-Fabris[2], Thomas Herrmannsdörfer[2], and Jochen Wosnitza[2] — [1]University of Leipzig, Faculty of Physics and Earth Science, Linnéstrasse 5, 04103 Leipzig, Germany — [2]Dresden High Magnetic Field Laboratory, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany

We report on the first resolved nuclear magnetic resonance (NMR) measurement of different chemical shifts in pulsed magnetic fields at the Dresden High Magnetic Field Laboratory (Hochfeld-Magnetlabor Dresden). After having minimized the field inhomogeneity across our sample volume down to 35 ppm by reducing the sample dimensions to 0.5 mm in all directions, resolved ^{19}F spectra of a mixture of hexafluorobenzene and benzotrifluoride were observed, yielding a chemical shift difference of 100 ppm. The scaling of the NMR linewidth with the sample size indicates that the linewidth is determined by spatial variation of the applied field over the sample volume. Thus, it is expected that one can further increase the resolution by reducing the sample dimensions. The spectra are demodulated using our recently demonstrated full understanding of the time dependence of NMR signals in pulsed magnetic fields up to 62 Tesla.

CPP 15.12 Tue 18:15 Poster A

Applicability of local thermal analysis using heatable AFM probes with respect to environmental influences for monitoring polymer surface properties — •Martin Laher, Thomas Fischinger, and Sabine Hild — Institut für Polymerwisschaften, Johannes Kepler Universität Linz

Local thermal analysis (LTA) in the nanometer scale has nowadays become a commercial add-on for atomic force microscopes. Heatable cantilever probes with tip radii below 50 nm provide the possibility to perform LTA measurements at defined surface positions with nanometer resolution. On condition that an appropriate tip-temperature calibration has been conducted, phase transition temperatures can be measured. Modification processes like solvent treatment or plasma activation are proposed to change thermo-mechanical properties. In this study, LTA is used to investigated the influence of activation parameters like plasma power or treatment time in softening temperatures on a close to surface region. It has been shown that for time dependent effects like solvent evaporation from swollen polymer surface layers there is an influence of one LTA measurement on subsequent ones. Point arrays of measurements show a thermal influence of each LTA on the surrounding area of several microns which decreases resolution. Supplying additional thermal energy to the sample with an external heater

reveals that LTA does not probe softening temperatures but rather the amount of thermal energy transferred. Force distance measurements of mechanical properties are compared to thermal LTA results.

CPP 15.13 Tue 18:15 Poster A

The Interaction of Carbon Dioxide with Water Molecules: DFT-based Path-Metadynamics — •Grégoire Gallet[1], Fabio Pietrucci[1], and Wanda Andreoni[1,2] — [1]Centre Européen de Calcul Atomique et Moléculaire, École Polytechnique Fédérale de Lausanne, Switzerland — [2]Institut de Théorie des Phénomènes Physiques, École Polytechnique Fédérale de Lausanne, Switzerland

We present an extensive study of the formation and dissociation of reactions $CO_2 + nH_2O \leftrightarrows H_2CO_3 + (n-1)H_2O$ in gas phase. We use both standard static approaches and path-metadynamics [1] to uncover the reaction mechanisms and to reconstruct the free energy surfaces. Our calculations are based on the pseudopotential/plane-wave implementation of the Kohn-Sham equations [2] and use several GGA and hybrid xc-functionals. Stringent validation tests of the computational methods were made and the performance of several xc-functionals was investigated. Excellent agreement was found among the different methods regarding the equilibrium and transition states configurations. Moreover, in spite of sizable differences in binding energies, all schemes agree in predicting the catalytic effect of water addition, also quantitatively. The role of entropy in determining the free energy barriers is critically investigated. [1] D. Branduardi, F.L. Gervasio and M. Parrinello; *J. Chem. Phys.*, **126**, 054103 (2007). [2] CPMD, *www.cpmd.org*; ©IBM Corp 1990-2012,©MPI für Festkörperforschung Stuttgart 1997-2001

CPP 15.14 Tue 18:15 Poster A

Electrical fine tuning of liquid crystal lasers — •Jürgen Schmidtke and Heinz-Siegfried Kitzerow — Department Chemie, Universität Paderborn, Germany

We demonstrate high-precision, continuous, electrical tuning of a photonic band-edge laser based on a dye-doped cholesteric liquid crystal. A micro-patterned array of electrodes creates an electric field perpendicular to the cholesteric helix, which distorts the chiral order of the liquid crystal, thus shifting the resonant band edge modes. This configuration allows for smooth tuning of the laser emission in a wavelength range of about 4 nm, using low voltages (of the order of 10 V).

CPP 15.15 Tue 18:15 Poster A

Revised self-consistent continuum solvation in electronic-structure calculations — Oliviero Andreussi[1], •Ismaila Dabo[2], and Nicola Marzari[1] — [1]Theory and Simulation of Materials, École Polytechnique Fédérale de Lausanne — [2]CERMICS, Project-team INRIA Micmac, Université Paris-Est

The solvation model proposed by Fattebert and Gygi [1] and Scherlis et al. [2] is reformulated, overcoming some of the numerical limitations encountered and extending its range of applicability. The resulting self-consistent continuum solvation (SCCS) [3] model provides a very effective and compact fit of computational and experimental data, whereby the static dielectric constant of the solvent and one parameter allow to fit the electrostatic energy provided by the PCM model with a mean absolute error of 0.3 kcal/mol on a set of 240 neutral solutes. Two parameters allow to fit experimental solvation energies on the same set with a mean absolute error of 1.3 kcal/mol. A detailed analysis of these results, broken down along different classes of chemical compounds, shows that several classes of organic compounds display very high accuracy, with solvation energies in error of 0.3-0.4 kcal/mol, whereby larger discrepancies are mostly limited to self-dissociating species and strong hydrogen-bond forming compounds.

[1] J. L. Fattebert and F. Gygi, J. Comput. Chem. 23, 662 (2002).

[2] D. A. Scherlis, J. L. Fattebert, F. Gygi, M. Cococcioni, and N. Marzari, J. Chem. Phys. 124, 074103 (2006).

[3] O. Andreussi, I. Dabo and N. Marzari, submitted to J. Chem. Phys.

CPP 15.16 Tue 18:15 Poster A

Generation of excited electron pulses by silicon–silicon oxide–platinum devices — •Michael Scheele and Detlef Diesing — Fakultät für Chemie, Universität Duisburg-Essen, 45117 Essen, Germany

Thin layer systems as the employed silicon–silicon oxide–platinum devices are used in studies of surface chemical reactions. In socalled chemicurrent measurements the tunneling current of the top electrode through the insulating oxide to the back electrode is monitored in the course of exothermic surface reactions. On the other hand one can push electrons of the back electrode to the top electrode by help of a bias voltage U. These electrons may induce surface reactions due to their intrinsic excess energy $e \cdot U$. This approach has barely been used yet. The pulsed voltage technique allows the injection of e.g. $3 \cdot 10^{12} e^-$ with a pulse voltage of 4 V for a pulse length of 1 ms. In a first experiment the hot electron induced heating of the top electrode (20 nm platinum) is characterized. The top electrode temperature is accessible simultaneously by measuring the resistivity of the top platinum film. One can thus discriminate between heating and excitation induced effects in surface chemical experiments. The possibility to desorb molecules or induce reactions by use of voltage pulses will provide a new kind of electrocatalyst.

CPP 15.17 Tue 18:15 Poster A

Field-cycling NMR based analysis of the damage structure in Ionic crystals irradiated with swift heavy ions irradiated with swift heavy ions — •Michael Ditter, Simon Quittek, and Franz Fujara — Institut für Festkörperphysik, TU Darmstadt

Radiation damage in ionic crystals such as lithium fluoride has been extensively studied in the past, however so far no heavy ion irradiated samples were examined with field-cycling (FC) NMR. In lithium fluoride the nuclear spin lattice relaxation time is decisively influenced by the presence of paramagnetic impurities and defects like F-centers, induced by swift heavy ion irradiation. Most of these defects are concentrated in a halo around the ion tracks. Besides defects created directly by the projectiles secondary radiation, originating during the stopping process inside the crystal, causes damage beyond the ion range. For the full examination of this effect a spatial resolution, as offered by one of our FC spectrometers, is desirable. The distribution of the defects is thought to be mainly responsible for the observed magnetic field dependence of the relaxation rate. Thus NMR relaxometry, especially field-cycling techniques, is a suitable tool to gather information about the structure of radiation damage. Additionally NMR spectroscopy can be used to detect the presence of molecular fluorine and lithium colloids in the damaged zones. Our results obtained by these methods will be presented.

CPP 15.18 Tue 18:15 Poster A

Improving the performance of liquid crystal lasers by electric fields — •Jürgen Schmidtke, Lu Lu, and Heinz-Siegfried Kitzerow — Department Chemie, Universität Paderborn, Germany

During the past decade, self-assembled photonic band edge lasers based on dye-doped cholesteric liquid crystals have attracted considerable interest as tunable, miniature light sources. We demonstrate that the lasing threshold and slope efficiency of a liquid crystal laser can be improved by application of an electric field: Using a dye-doped cholesteric liquid crystal with negative dielectric anisotropy as the DFB laser structure, emission characteristics improves with increasing ac electric field along the cholesteric helix. Possible reasons are a partial suppression of thermally driven director fluctuations, as well as a stabilization of the planar cholesteric texture against disturbances by the optical pumping process.

CPP 15.19 Tue 18:15 Poster A

Design and Characterization of a Gas Sensor System Consisting of a Poly(amide-imide) and Cryptophane-A Covered Optical Fiber — Carmen M. Gonzalez Henriquez[1], •Ulrich G. Volkmann[1], Marcelo Cisternas[1], Rosario Ortega[1], Mauricio Sarabia[1], Patrick Huber[1], and Alvaro Henriquez[2] — [1]Surface Lab — [2]Plasma and Optics Lab, Facultad de Física, Pontificia Universidad Católica de Chile, Chile

The principal innovation of this project is the design of a gas sensor based on the usage of a mixture between poly(amide-imide) oligomer [1] as matrix and cryptophane-A [2] covering an optical fiber. The optical behavior of this system was studied upon adsorption of different gases, typical of the decomposition of organic matter: CO2, N2, CH4 and H2. Using ellipsometry in a modified PCSA-null setup, we detect large changes in the optical polarization as a function of gas pressure or concentration.

[1] Carmen M. Gonzalez Henriquez et al. Structural symmetry breaking of silicon-containing poly(amide-imide) oligomers and its relation to electrical conductivity and Raman-active vibrations. *Polymer Int* **(2011)**, DOI: 10.1002/pi.3169.

[2] Suozhu Wu et al. Mode-filtered light methane gas sensor based on cryptophane A. *Analytica Chimica Acta* **(2009)**, 633 (2), 238-243.

C.M. Gonzalez Henriquez acknowledges a scholarship from VRI Nr. 10/2010 (PUC). Work supported by FONDECYT project Nr. 1100882.