9th International Conference
on BROADBAND DIELECTRIC SPECTROSCOPY AND ITS APPLICATIONS

Joint Meeting of
The 9th Conference
of The International Dielectric Society
&
The 15th Conference
on Dielectric And Related Phenomena

September 11 – 16, 2016
Pisa (Italy)

Programme
& Book of Abstracts

Edited by M. Labardi & E. Tombari

We kindly acknowledge the group of Prof. M. Paluch, Institute of Physics, University of Silesia, Katowice, Poland for the template of the book of abstracts.

PREFACE

Broadband dielectric spectroscopy (BDS) is a powerful method for investigation of molecular dynamics of various materials. It enables to study molecular mobility through the observation of relaxation processes over a wide frequency range up to 16 decades, at different temperatures and pressures. BDS finds application in many fields of science and technology. It is successfully employed in studies on (i) molecular dynamics of liquids, liquid crystals, glasses, polymers, disordered crystals; (ii) charge transport in ionic glasses and liquids, semiconductors, organic crystals, ceramics, polymers; (iii) interfacial phenomena and confinement effects; (iv) non-linear electrical effects. BDS is also a very useful tool to monitor chemical reactions and phase transitions, e.g. crystallization. Consequently, numerous basic and applied topics can be studied by dielectric techniques. The BDS2016 conference will provide a platform to discuss these exciting developments.

In detail, the following topics will be addressed in devoted sessions:

S01 Water and Hydrogen Bonded Systems
S02 Polymer Dynamics
S03 Terahertz Spectroscopy
S04 BDS of Phase Transitions and Dynamics in Amorphous, Partially Ordered and Ordered Systems (Liquid and Plastic Crystals, Ferroelectrics, Ceramics, Pharmaceuticals, etc.)
S05 Glassy Dynamics and its Scaling under Different Variables (Pressure, Temperature, Electric Fields, etc.)
S06 Non-Linear Electrical Effects
S07 Investigation of Interfacial Phenomena and Confinement Effects
S08 Dielectric Spectroscopy Spatially Resolved at Micro- and Nanoscale
S09 BDS Applied to Life Science
S10 Charge Transport and Relaxation

Additionally a Forum Discussion on “Water and Related Dielectric Phenomena” will take place, as well as the Industry Forum **(IF)**, a special session devoted to Industrial Applications of BDS.
Finally, the Technical Session **(TS)** will focus to new experimental setup and analysis tools available on the market.

ORGANIZING COMMITTEE

The conference is organized and supported by the Institute for Chemical and Physical Processes (CNR-IPCF) in Pisa and by the Physics Department of the University of Pisa (Italy).

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Università di Pisa, Italy

Elpidio Tombari
CNR-IPCF, Italy

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ACKNOWLEDGEMENTS

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Programme of the 9th International Conference on Broadband Dielectric Spectroscopy and its Applications, CNR Campus, Pisa, Italy, September 11-16, 2016 (BDS 2016)

Sunday 11th September		Monday 12th September		Tuesday 13th September		Wednesday 14th September		Thursday 15th September		Friday 16th September	
8:30 ↓ 14:00		**O-1 ↓ O-4**	**S01** **Chairman:** **Friedrich Kremer**	**O-21 ↓ O-25**	**S06** **Chairman:** **Bernhard Roling**	**O-38 ↓ O-42**	**S07** **Chairman:** **Michael Wübbenhorst**	**O-59 ↓ O-63**	**S07** **Chairman:** **Andreas Schönhals**	**O-76 ↓ O-80**	**S10** **Chairman:** **Alexei Sokolov**
		8:30	**Welcome (20)**	8:30	William Coffey (30)	8:30	Friedrich Kremer (30)	8:30	Michael Wübbenhorst(30)	8:30	Zaneta Wojnarowska(30)
		8:50	Juan Colmenero (30)	9:00	Francois Ladieu (30)	9:00	Simone Napolitano (30)	9:00	Wilhelm Kossack (20)	9:00	Catalin Gainaru (30)
		9:20	Ivan Popov (20)	9:30	Ranko Richert (30)	9:30	Koji Fukao (20)	9:20 9:40	Anna Panagopoulou (20) Martin Tress (20)	9:30	Falk Frenzel (20)
		9:40	Roland Böhmer (30)	10:00	Michal Rajnak (20)	9:50	Laurent Delbreilh (20)	10:00	Nora Konnertz(20)	9:50	Pit Sippel (20)
		10:10	Sebastian Pawlus (20)	10:20	Anthony West (20)	10:10	Sherif Madkour (20)	10:20	**Awards: Debye Prize & Posters**	10:10	Alberto Rivera-Calzada (20)
		10:30	**Coffee break**	10:40	**Coffee break**	10:30	**Coffee break**	10:30	**Coffee break**	10:30	**Coffee break**
		O-5 ↓ O-9	**S02** **Chairman:** **Tiberio Ezquerra**	**O-26 ↓ O-30**	**S05** **Chairman:** **Mike Roland**	**O-43 ↓ O-47**	**S05 & S07** **Chairman:** **Kia L. Ngai**	**O-64 ↓ O-67**	**S07** **Chairman:** **Marian Paluch**	**O-81 ↓ O-85**	**S10** **Chairman:** **Anatoli Serghei**
		11:00	Marina Guenza (30)	11:10	Marian Paluch (30)	11:00	Gyan P. Johari (30)	11:00	Andreas Schönhals (30)	11:00	Tyler Cosby (30)
		11:30	Krzysztof Halagan (30)	11:40	Kristine Niss (30)	11:30	Carlos Leon (30)	11:30	Ernst Rössler (30)	11:30	Andrea Moguš-Milanković (20)
		12:00	Didier Long (20)	12:10	Vladimir Novikov (20)	12:00	M. Jasiurkowska-Delaporte (20)	12:00	Kia L. Ngai (30)	11:50	Jean-Claude Badot (20)
		12:20	Michelina Soccio (20)	12:30	Andrzej Grzybowski (20)	12:20	Kamil Kaminski (20)	12:30	Alexei Sokolov (30)	12:10	Bernhard Roling (30)
		12:40	William H. Woodward (20)	12:50	Allisson Saiter (20)	12:40	Magdalena Tarnacka (20)			12:40	Junichi Kawamura (20)
		13:00	**Lunch**	13:10	**Lunch**	13:00	**Lunch**	13:00	**Lunch**	13:00	**Lunch**

Sunday 11th September		Monday 12th September		Tuesday 13th September		Wednesday 14th September		Thursday 15th September		Friday 16th September	
14:00 ↓ 18:40	**Registration & Tutorials for students**	**O-10 ↓ O-14**	**S03** **Chairman: Giuseppe Annino**	**O-31 ↓ O-34**	**S01** **Chairman: Naoki Shinyashiki**	**O-48 ↓ O-52**	**TS & IF** **Chairman: S.Capaccioli & F. Kremer**	**O-68 ↓ O-72**	**S08** **Chairman: Juan Colmenero**	**O-86 ↓ O-89**	**S10** **Chairman: Simone Capaccioli**
		14:20	Alexander Shkurinov (30)	14:20	Paul Ben Ishai (30)	14:20	Giovanni D'Amore - Keysight (20)	14:20	Mike Roland (30)	14:20	Rudolf Hilfer (20)
		14:50	J. Alex Zeitler (30)	14:50	George Floudas (30)	14:40	Dirk Wilmer - Novocontrol	14:50	Tiberio A. Ezquerra (30)	14:40	N. S. Krishna Kumar (20)
		15:20	Keisuke Tominaga (20)	15:20	Yuri Feldman (30)	15:00	Jens Wallauer - RHD (20)	15:20	Daniel Martínez-Tong (20)	15:00	Anatoli Serghei (30)
		15:40	Sebastian Emmert (20)	15:50	Ryusuke Nozaki (30)	15:20 15:40	E. Logakis (20) Martin Engel (20)	15:40	Massimiliano Labardi (20)	15.30	Gunnar A. Niklasson (20)
		16:00	Boris Gorshunov (20)			16:00	**Industry Forum Discussion (40)**	16:00	Georg Gramse (20)	15:50	**Closing Remarks (10)**
		16:20 ↓ 17:20	**Poster Session S01 → S04 (P-1 → P-29) & Coffee break**	16:20 ↓ 16:50	**Coffee break**	16:40 ↓ 17:40	**Poster Session S05 → S10 (P-30 → P-62) & Coffee break**	16:20 ↓ 16:50	**Coffee break**	16:00	**End of the Conference**
16:30 ↓ 19:00	**Welcome Party**	**O-15 ↓ O-20**	**S04 & S05** **Chairman: Elpidio Tombari**	**O-35 ↓ O-37**	**S01** **Chairman: George Floudas**	**O-53 ↓ O-58**	**S04** **Chairman: Ranko Richert**	**O-73 ↓ O-75**	**S09** **Chairman: Yuri Feldman**		
		17:20	Ferid Salehli (20)	16:50	Silvina Cerveny (30)	17:40	Yue Zhang (20)	16:50	Roland Netz (30)		
		17:40	Roberto Macovez	17:20	Naoki Shinyashiki (20)	18:00	Madalena Dionísio (20)	17:20	Katia Grenier (20)		
		18:00	Daniel Reuter (20)	17:40	Apostolos Kyritsis (20)	18:20	K.Grzybowska(20)	17:40	Masahiro Nakanishi (20)		
		18:20	Li-Min Wang (20)	18:00 ↓ 19:00	Forum: “Water and Dielectric Phenomena” (Chairman: Yuri Feldman)	18:40	Karolina Adrjanowicz (20)				
		18:40	Satya Tripathy (20)			19:00	Natália Correia (20)	18:00	**Visit to “Certosa di Calci”**		
		19:00	Shimon Lerner (20)	18:30 -20:00	**Tour across Pisa 1th group (90)**	19:20	Miroslaw Galazka (20)	19:00	**Piano & Violin Concert**		
		20:30 ↓ 22.30	**Special Dinner for Key Speakers and IDS Board memb.**	19:00 ↓ 20:30	**Tour across Pisa 2nd group (90)**	19:40 ↓ 21:30	**IDS Board Meeting** (& Dinner)	20:30 ↓ 22:30	**Conference Dinner**		

Programme
of the 9th International Conference on Broadband Dielectric Spectroscopy and its Applications, CNR Campus, Pisa, Italy, September 11-16, 2016

SUNDAY

Atrium - **Welcome and participant kit delivery**, 14:00 – 18.40

Room 27 - **Dielectric Tutorials for students**, 14:00 – 18:40

14:00 **Broadband Dielectric Spectroscopy (BDS) - Basics and Selected Application**
Andreas Schönhals

14:50 **Nuclear Magnetic Resonance (NMR) – Basics and Comparison with BDS**
Roland Böhmer

15:40 **Local Dielectric Spectroscopy by Scanning Probes**
Massimiliano Labardi

Coffee break, 16:30 – 17.00

17:00 **Techniques of Time-Resolved Dielectric Relaxation Measurements in the Nonlinear Regime**
Ranko Richert

17:50 **High Pressure Dielectric Spectroscopy**
Marian Paluch

Room 29 - **Welcome party**, 16:00 – 19:00

MONDAY

8:30 **Welcome**

Session S01: Water and Hydrogen Bonded Systems, 8:50 – 10.30

Chairman: Friedrich Kremer

8:50 **Dielectric susceptibility of Liquid water: microscopic insights from neutron scattering and MD-simulations**
O-1
J. Colmenero

9:20 **The mechanism of the dielectric relaxation in water**
O-2 I. Popov, P. Ben Ishai, A. Khamzi, Y. Feldman

9:40 **Mixing effects on the structure and dynamics of monohydroxy alcohols**
O-3
S. P. Bierwirth, T. Büning, J. Lueg, C. Sternemann, C. Gainaru, M. Tolan, R. Böhmer

10:10 **Are there possibilities to learn something new from pressure studies of primary alcohols?**
O-4
S. Pawlus, M. Wikarek, S.N. Tripathy and M. Paluch

Coffee break, 10:30 – 11.00

Session S02: Polymer Dynamics, 11:00 – 13.00

Chairman: Tiberio Ezquerra

11:00 **Intra- and Intermolecular Contributions to the Dynamics of Polymer Melts**
O-5
M. Guenza

11:30 **Diffusion in Complex Polymer Systems Modeled with Cooperative Dynamics and The Dedicated Simulator**
O-6
K. Halagan, P. Polanowski, J. Jung, M. Kozanecki, J. Ulanski

12:00 **Heterogeneous dynamics and plasticity of a stretched polymer glass studied by dielectric spectroscopy**
O-7
R. Pérez-Aparicio, D. Cottinet, C. Crauste-Thibierge, L. Vanel, P. Sotta, J.Y. Delannoy, D.R. Long, S. Ciliberto

12:20 **Structure-dynamics relationship in biobased polyesters**

O-8 **of 1,3-propanediol as revealed by dielectric spectroscopy**
M. Soccio, L. Genovese, A. Linares, N. Lotti, A. Munari, A. Szymczyk, Z. Roslaniec, A. Nogales, T.A. Ezquerra

12.40 **Insights into the Relaxations of Hydroxypropyl**
O-9 **Methylcellulose via Broadband Dielectric Spectroscopy**
W.H.H. Woodward, T. Chatterjee, M. Lesniak, T. McIntire, K. O'Donnell, B. Sammler, K. Kearns, D. Meunier, Y. Li

Lunch, 13:00 – 14:20

Session S03: Terahertz Spectroscopy, 14:20 – 16.20
Chairman: Giuseppe Annino

14:20 **Interaction of high-intense femtosecond radiation with**
O-10 **gas medium and gas cluster beams: generation of the high intesity THz and X-ray radiation and their applications**
A.V.Balakin, M.S.Dzhidzhoev, V.M.Gorgienko, M.N.Esaulkov, I.A.Zhvaniya, I.A.Kotelnikov, N.A.Kuzechkin, I.A.Ozheredov, A.B.Savel'ev, A.Yu.Sidorov, P.M.Solyankin, M.B. Smirnov, A.P. Shkurinov

14:50 **The role of the JG β-Relaxation for the physical stability**
O-11 **of organic molecular glasses – new insights from THz-TDS measurements and molecular dynamics simulations**
M.T. Ruggiero, J.A. Zeitler

15:20 **Broadband Dielectric Spectrocopy from MHz to THz on**
O-12 **Proteins; Comparison between Globular Proteins and Membrane Proteins**
N. Yamamoto, S. Ito, K. Ohta, E. Chatani, H. Kandori, K. Tominaga

15.40 **Boson Peak and Fast Dynamics of Glassy Matter**
O-13 S. Emmert, P. Lunkenheimer, A. Loidl

16.00 **Terahertz spectroscopy of incipient ferroelectric state of**
O-14 **nanoconfined water molecules**
B. Gorshunov, V. Torgashev, E. Zhukova, M. Belyanchikov, V. Thomas, M. Savinov, C. Kadlec, F. Kadlec, A. Prokhorov,

L. Kadyrov, J. Petzelt, T. Ostapchuk, D. Fursenko, P. Thomas, G. Shakurov, M. Dressel

Coffee break & Poster Session S01 → S04 (P-1 to P-29),
16:20 – 17.20

Session S04: Broadband Dielectric Studies of Phase Transitions and Dynamics in Amorphous, Partially Ordered and Ordered Systems (Liquid and Plastic Crystals, Ferroelectrics, Ceramics, Pharmaceuticals, etc.)
17:20 – 18.20

Chairman: Elpidio Tombari

17.20 **Dielectric relaxation in self-assembled diphenylalanine nanotubes**
O-15 F. Salehli, S. Kopyl, A. Kholkin

17.40 **Dynamics in translationally ordered solids**
0-16 R. Macovez, M. Romanini, P. Tripathi, M. Zachariah, M. del Barrio, J.L. Tamarit

18.00 **Ionic and dipolar dynamics in binary plastic crystalline systems**
O-17 D. Reuter, K. Geirhos, P. Lunkenheimer, A. Loidl

Session S05: Glassy Dynamics and its Scaling under Different Variables (Pressure, Temperature, Electric Fields, etc.),
18:20 – 19.20

Chairman: Elpidio Tombari

18.20 **An unique secondary relaxation in the rigid glass forming molecular liquid of 1-methylindole**
O-18 L.M. Wang, X. Li, Wenkang Tu, S. Capaccioli, K.L. Ngai

18.40 **Spatially Heterogeneous Nature of Secondary β-Relaxation**
O-19 S.N. Tripathy, M. Rams-Baron, Z. Wojnarowska, J. Knapik, M. Paluch

19.00 **Entropy-Enthalpy Compensation in Glass Formers**
O-20 S.E. Lerner, P. Ben Ishai, Y. Feldman

Dinner for Key Speakers and Members of IDS Board, 20:30 – 22:30

TUESDAY

Session S06: Non-Linear Electrical Effects, 8:30 – 10.40

Chairman: Bernhard Roling

8:30 **External dc bias field effects in the nonlinear ac stationary response of dipolar particles in a mean field potential**
O-21 W.T. Coffey, N. Wei, Pi.M. Déjardin, Y.P. Kalmykov

9:00 **Fifth-order susceptibility unveils the growth of thermodynamic amorphous order in glass-formers**
O-22 S. Albert, Th. Bauer, M. Michl, G. Biroli, J.-P. Bouchaud, A. Loidl, P. Lunkenheimer, R. Tourbot, C. Wiertel-Gasquet, F. Ladieu

9:30 **Tuning the Entropy of Dielectrics by High DC Fields: Experiments and Models**
O-23 R. Richert

10:00 **Dielectric spectroscopy and neutron scattering study of colloidal magnetic fluids in electric fields**
O-24 M. Rajnak, M. Timko, P. Kopcansky, K. Paulovicova, B. Dolnik, J. Kurimsky, V. Petrenko, M. Avdeev, A. Feoktystov

10:20 **Field-sensitive electrical properties of oxide ceramics: dielectric breakdown and resistive switching, a common mechanism?**
O-25 A.R. West

Coffee break, 10:40 – 11.10

Session S05: Glassy Dynamics and its Scaling under Different Variables (Pressure, Temperature, Electric Fields, etc.), 11:10 – 13.10

Chairman: Mike Roland

11:10 **Dielectric Relaxation of Supercooled Van der Waals Liquids – Universal Pattern of Behavior**
O-26
M. Paluch

11:40 **Extracting new information from dielectric spectroscopy by keeping track of geometric changes of the capacitor**
O-27
K. Niss

12:10 **Qualitative change in structural dynamics of some glass-forming systems**
O-28
V.N. Novikov, A.P. Sokolov

12:30 **Entropic models and their prospects for an universal description of dielectric phenomena near the glass transition**
O-29
A. Grzybowski, S. Mroz, E. Masiewicz, K. Grzybowska, S. Pawlus, M. Paluch

12:50 **Segmental mobility at the glass transition in poly(ethylene-vinyl acetate) copolymers : Comparison of two approaches**
O-30
B. Rijal, J. A. Soto Puente, L. Delbreilh, K. Fatyeyeva, E. Dargent1, A. Saiter

Lunch, 13:10 – 14:20

Session S01: Water and Hydrogen Bonded Systems, 14:20 – 16.20

Chairman: Naoki Shinyashiki

14:20 **Ultra-confinement: The Mysteries of Ancient Water Imprisoned in sub-nano channels in Natural Minerals**
O-31
P. Ben Ishai

14:50 O-32	**Water confined in nanoporous alumina: Ice nucleation, Kinetics and Dynamics** Y. Suzuki, Y. Yao, M. Steinhart, H.-J. Butt, G. Floudas
15:20 O-33	**The interplay between water and solute** Y. Feldman
15.50 O-34	**Dielectric Study of Aqueous Solutions of Collagen Extracted from Tilapia Scale** S. Kuwaki, H. Kawamata, T. Ikoma, J. Tanaka, R. Nozaki

Coffee break 16:20 – 16:50

Session S01: Water and Hydrogen Bonded Systems
16:50 – 18.00

Chairman: George Floudas

16:50 O-35	**Dynamical and Structural Study of n-Lysine´s Oligomers** S. Cerveny
17:20 O-36	**Dynamics of water, solute, and ice in partially crystallized aqueous solutions studied by broadband dielectric spectroscopy** N. Shinyashiki, K. Sasaki, R. Kita, S. Yagihara
17:40 O-37	**Water dynamics in Hyaluronic Acid hydrogels** A. Kyritsis, S. Kripotou, O. Vassiliadou, L.O. Cervelló, A. Vallés-Lluch, M.M. Pradas

Discussion Forum: “Water and Related Dielectric Phenomena” 18:00 – 19.00

Chairman: Yuri Feldman

Tour across Pisa 1th group 18:30 – 20:00

Tour across Pisa 2th group 19:00 – 20.30

WEDNESDAY

Session S07: Investigation of Interfacial Phenomena and Confinement Effects, 8:30 – 10.30

Chairman: Michael Wübbenhorst

8:30 **Molecular dynamics in nanometric confinement**
O-38 F. Kremer, W.K. Kipnusu, N. Neubauer, E.U. Mapesa, M. Tress

9:00 **Non-equilibrium kinetics of the segmental dynamics of 1D confined polymer melts**
O-39 S. Napolitano, A. Panagopoulou

9:30 **Electrode Polarization and Glassy Dynamics in Thin Films of Polyamide Random Copolymers**
O-40 K. Fukao, N. Taniguchi, P. Sotta, D. Long

9:50 **Effect of Confinement on Segmental Relaxations in PBAC/PETg Multi-layered Films**
O-41 B. Rijal, L. Delbreilh, D. Prevosto, R. Adhikari, E. Baer, E. Dargent, A. Saiter

10:10 **Dielectric and Thermal Relaxation Behavior of Ultra-Thin Films of Poly(vinyl methyl ether) – Evidence of an Adsorbed Layer**
O-42 S. Madkour, P. Symoniak, A. Schönhals

Coffee break, 10:30 – 11.00

Session S05: Glassy Dynamics and its Scaling under Different Variables (Pressure, Temperature, Electric Fields, etc.), 11:00 – 11:30

Chairman: Kia L. Ngai

11:00 **Some Overlooked Effects in Dielectric Phenomenon**
O-43 G.P. Johari

Session S07: Investigation of Interfacial Phenomena and Confinement Effects, 11:30 – 13:00

Chairman: Kia L. Ngai

11:30 **Atomic origin of barriers for ionic transport through interfaces**
O-44 M. A. Frechero, M. Rocci, G. Sánchez-Santolino, Amit Kumar, J. Salafranca, R. Schmidt, A. Rivera-Calzada, S. Jesse, S.T. Pantelides, S. V. Kalinin, M. Varela, S. J. Pennycook, J. Santamaria, C. Leon

12:00 **Intra and inter-molecular dynamics in poly(ethylene glycol) derivatives under confinement**
O-45 M. Jasiurkowska-Delaporte, W. Kossack, W.K. Kipnusu, J.R. Sangoro, C. Iacob, F. Kremer

12:20 **Peculiar behavior of the dynamics of confined liquids. The role of negative pressure**
O-46 K. Kaminski, M. Tarnacka, E.Kaminska , S. Pawlus, K. Adrjanowicz, K. Koperwas, W.K. Kipnusu, M. Paluch

12:40 **Studies on the Temperature and Time Induced Variation in the Molecular Dynamics of Low and High Molecular Weight Glass-Formers at the Nanoscale**
O-47 M. Tarnacka, K. Kaminski, E. Kaminska, M. Paluch

Lunch, 13:00 – 14:20

Technical Forum, 14:20 – 15.20
Chairman: Simone Capaccioli

14:20 **Devices and Material characterization from DC to mm-wave and THz**
O-48 G. D'Amore, S. Phommakesone (Keysight)

14:40 **Broadband Dielectric Spectroscopy – Technical Aspects of Today and Tomorrow**
O-49 D. Wilmer (Novocontrol)

15:00 **Extracting Differential Capacitance Values of the Ionic Liquid-Au(111) Interface from Impedance Data using the RelaxIS Impedance Spectrum Analysis Software**
O-50

J. Wallauer, M. Drüschler (RHD)

Industry Forum: Industrial Applications of Broadband Dielectric Spectroscopy, 15:20 – 16:40

Chairman: Friedrich Kremer

15:20 **High Voltage Dielectric Spectroscopy on LDPE films**
O-51 E. Logakis, T. Christen (ABB Corporate Research)

15:40 **Application of dielectric spectroscopy for the optimization of high performance liquid crystal mixtures**
O-52 M. Engel, M. Kraska, A. Götz, B. Stühn, G. Bernatz (Merck)

16:00 **Industry Forum Discussion**

Coffee break & Poster Session S05 → S10 (P-30 to P-62), 16:40 – 17.40

Session S04: Broadband Dielectric Studies of Phase Transitions and Dynamics in Amorphous, Partially Ordered and Ordered Systems (Liquid and Plastic Crystals, Ferroelectrics, Ceramics, Pharmaceuticals, etc.) 17:40 – 19.40

Chairman: Ranko Richert

17:40 **Dielectric Spectroscopy and Glass Transitions of Organic Molecules and Mixtures Prepared from Submicron Particle Deposition**
O-53 Y. Zhang, A. Lambe, T. Onasch, S. Katira, W. Xu, L. Renbaum-Wolff, M. Canagaratna, W. Brooks, W. Robinson, P. Kebabian, A. Freedman, J. Jayne, D. Worsnop, P. Davidovits, D. Chandler, C. Kob

18:00 **Probing the physical state and molecular mobility of naproxen drug confined to nanoporous silica matrices**
O-54 T. Cordeiro, A. F. M. Santos, G. Nunes, G. Cunha, J. C.

Sotomayor, I. Fonseca, F. Danede, C. J. Dias, M. M. Cardoso, N. T. Correia, M. T. Viciosa, M. Dionísio

18:20
O-55
Molecular factors governing the recrystallization of amorphous anti-inflammantory drug in mixtures with small and large excipients
K. Grzybowska, K. Chmiel, J. Knapik, A. Grzybowski, M. Paluch

18:40
O-56
Crystallization of glass-forming liquids studied in T-p space along different iso-invariant lines
K. Adrjanowicz, K. Koperwas, M. Paluch

19:00
O-57
Characterization of the crystalline/amorphous phases of SIMVASTATIN: contribution from TSDC and DRS techniques
N.T. Correia, M.T. Viciosa, H.P. Diogo, T.G. Nunes

19:20
O-58
Universal scaling of dielectric response of various liquid crystals and glass-forming liquids
M. Gałązka, M. Massalska-Arodź, E. Juszyńska-Gałązka, N. Osiecka, L. Calucci, E. Carignani, C. Forte, M. Geppi

IDS Board Meeting and Dinner, 19:40 – 21.30

THURSDAY

Session S07: Investigation of Interfacial Phenomena and Confinement Effects, 8:30 – 10.20

Chairman: Andreas Schönhals

8:30
O-59
Dielectric and ferroelectric behaviour of thin films of trialkylbenzene-1,3,5-tricarboxamide (BTA)
M. Wübbenhorst, A. V. Gorbunov, T. Putzeys, I. Urbanavičiūtė, R.A.J. Janssen, R. P. Sijbesma, M. Kemerink

9:00
Remanent polarisation and liquid crystal alignment in composite films of 5CB and 6CB in PVDF-TrFe

O-60 W. Kossack, L. Holländer, M. Kollosche, W. Wirges, R. Gerhard, F. Kremer

9:20 **Dielectric studies of collagen thin films**
O-61 A. Panagopoulou, S. Napolitano

9:40 **Crystallite growth enhances segmental dynamics in star-shaped semi-crystalline polymer**
O-62 M. Tress, M. Vielhauer, P. Lutz, R. Mülhaupt, F. Kremer

10:00 **Dielectric Investigations of the high Performance Polymer PIM-1 and Nanocomposites containing PhenethylPOSS**
O-63 N. Konnertz, M. Böhning, A. Schönhals

Debye Prize & Poster Sessions Winners, 10:20 – 10:30

Coffee break, 10:30 – 11.00

Sessions S07: Investigation of Interfacial Phenomena and Confinement Effects, 11:00 – 13.00
Chairman: Marian Paluch

11:00 **Behavior of Ultra-Thin Films of Blends of Polystyrene/ Poly(vinyl methyl ether) by Nanosized Relaxation Spectroscopy**
O-64 S. Madkour, P. Symoniak, A. Schönhals

11:30 **Dynamics of asymmetric binary glass formers**
O-65 B. Pötzschner, D. Bock, F. Mohamed, R.Kahlau, C. Bächer, E. Wagner, A. Lichtinger, K. Kreger, Ch. Neuber, H.W. Schmidt, E.A. Rössler

12:00 **Johari-Goldstein β-relaxation Mistaken for Confinement Effect in Highly Asymmetric Mixtures**
O-66 S. Valenti, S. Capaccioli, K.L. Ngai

12:30 **Unraveling Interfacial Dynamics in Polymer Nanocomposites sites**

O-67 A.P. Sokolov

Lunch, 13:00 – 14:20

Session S08: Dielectric Spectroscopy Spatially Resolved at Micro- and Nanoscale, 14:20 – 16.20

Chairman: Juan Colmenero

14:20 **Local, global, and particle dynamics in polypropylene glycol / silica nanocomposites**
O-68 C.M. Roland, M. Tyagi, R. Casalini

14:50 **Dielectric Relaxation and Electrical Conductivity of Poly(3-hexyltiophene) and its blends with fullerene: from bulk to thin films**
O-69 J. Cui, A. Nogales, Á. Rodríguez-Rodríguez, M.C. García-Gutiérrez, E. Rebollar, T.A. Ezquerra

15:20 **Exploring interfacial polarization phenomena in semicrystalline polymer thin films: from local to bulk dielectric measurements**
O-70 D. E. Martínez-Tong, L.A. Miccio, A. Alegría

15.40 **Broadband Local Dielectric Spectroscopy**
O-71 M. Labardi, M. Lucchesi, D. Prevosto, S. Capaccioli

16:00 **Nanoscale complex impedance and dielectric properties of single CHO cells and E.coli bacteria at GHz frequencies by scanning microwave microscopy**
O-72 G. Gramse, S.S. Tuca, M.C. Biagi, R. Fabregas, M. Hofstadt, G. Badino, E. Brinciotti, M. Kasper, Y.J. Oh, R. Zhu, C. Rankl, A. Juárez, P. Hinterdorfer, L. Fumagalli, G. Gomila, F. Kienberger

Coffee break, 16:20 – 16:50

Session S09: Broadband Dielectric Spectroscopy Applied to Life Science , 16:50 – 18.00

Chairman: Yuri Feldman

16:50 **Water contribution to the dielectric spectra of electrolytes and proteins**
O-73 R.R. Netz

17:20 **Microwave dielectric spectroscopy of alive single human cells**
O-74 K. Grenier, T. Chen, W. Chen, A. Zedek, J.J. Fournié, M. Poupot, D. Dubuc

17:40 **Dynamics of Water Molecules Absorbed into Stratum Corneum**
O-75 M. Nakanishi, A. Greenbaum (Gutina) , Y. Domanov, F. Formanek, B. Querleux, Y. Feldman

Visit to "Certosa di Calci" 18:00 – 19.00

Piano Concerto, 19:00 – 20.30

Conference dinner, 20:30 – 22:30

FRIDAY

Sessions S10: Charge Transport and Relaxation, 8:30 – 10.30
Chairman: Alexei Sokolov

8:30 **Effect of Compression on the Ion Conduction in Polymerized Ionic Liquid**
O-76 Z. Wojnarowska, J. Knapik, M. Diaz, A. Ortiz, M. Paluch, V. Bocharova, A. Sokolov

9:00 **Ionic relaxation process connecting both local and macroscopic charge dynamics in conducting materials**
O-77 V. Bocharova, V. Novikov, R. Böhmer, A.P. Sokolov, C. Gainaru

9:30 **Molecular dynamics, charge transport and mesoscopic structure in Polymeric Ionic Liquids (PILs)**
O-78 F. Frenzel, M. Y. Folikumah, M. Schulz, A. M. Anton, W.H.

Binder, F. Kremer

9:50 **Conductivity and relaxation dynamics of ionic liquids**
O-79 P. Sippel, P. Lunkenheimer, S. Krohns, E. Thoms, A. Loidl

10:10 **The ionic liquid gating process of YBCO EDLT probed by Dielectric Spectroscopy**
O-80 A. Rivera-Calzada, A. Perez-Muñoz, C. Leon, J. Santamaria, J. Garcia-Barriocanal

Coffeee break, 10:30 – 11.00

Session S10: Charge Transport and Relaxation, 11:00 – 13.00
Chairman: Anatoli Serghei

11:00 **Proton Transport in Imidazoles: Unraveling the Role of Supramolecular Structure**
O-81 T. Cosby, J.R. Sangoro

11:30 **Electrical Mobility of Lithium ions in Boro-germano-phosphate Glasses**
O-82 A. Moguš-Milanković, K. Sklepić, R.D. Banhatti, P. Mošner, L. Koudelka, G. Tricot

11:50 **Contribution of the dielectric spectroscopy to the multiscale study of the electrode materials**
O-83 J.C. Badot, O. Dubrunfaut, B. Lestriez

12:10 **Li^+ Transference Numbers in Liquid Battery Electrolytes obtained by Very-low-frequency Impedance Spectroscopy**
O-84 B. Roling, F. Wohde, M. Balabajew

12:40 **Deviation from Scaling Law and Excess Dielectric Loss in Mixed Alkali Glasses**
O-85 J. Kawamura, Y. Takayanagi, N. Kuwata

Lunch, 13:00 – 14.20

Session S10: Charge Transport and Relaxation, 14:20 – 15.50
Chairman: Simone Capaccioli

14:20 O-86
Generalized Theory of Dielectric Response in Disordered Media with Heterogeneities on Multiple Spatial Scales
R. Hilfer

14:40 O-87
Complex Current Analysis for the Description of Combined Conduction and Dielectric Relaxation Processes in Solids
N.S.K. Kumar, G. Govindaraj

15:00 O-88
Electrode polarization vs. Maxwell-Wagner-Sillars interfacial polarization: characteristic frequencies, scaling laws, and applications
A. Serghei, M. Samet, G. Boiteux, A. Kallel

15.30 O-89
Ageing of electrochromic tungsten oxide thin films studied by impedance spectroscopy
G.A. Niklasson, S. Malmgren, S. Green, C.G. Granqvist

Closing Remarks, 15:50 – 16:00

POSTER PRESENTATIONS

MONDAY: 16:20 – 17:20

Session S01: Water and Hydrogen Bonded Systems

P-1 **Dielectric relaxation time of ice Ih in partially crystallized aqueous polymer mixtures**
K. Sasaki, T. Yasuda, Y. Matsui, R. Kita, S. Yagihara, and N. Shinyashiki

P-2 **Homopolyaminoacid Dynamics in Aqueous Solution**
I. Combarro-Palacios, A.l Alegría, J. Swenson, S. Cerveny

P-3 **Novel Concept of Non-Debye Dipole for the Description of Dielectric Relaxation in glassy 2-Ethyl-1-Hexanol and Glycerol**
G. Govindaraj

P-4 **Influence of hydratation and heat treaments on dielectric properties of wheathered granite**
S. Araujo, L. Delbreilh, R. Antoine, E. Dargent, C. Fauchard

P-5 **Space-time dynamics in water**
V.G. Artemov, A.A. Volkov (Jr.), N.N. Sysoev, A.A. Volkov

P-6 **Application of Broadband Dielectric Spectroscopy to Cultural Heritage: characterization and preservation of ancient paper artwork**
M. Fomina, A. Cupane

P-7 **Hydration shell dynamics driven by protein interface**
A. Greenbaum (Gutina), Y. Kurzweil-Segev, I. Popov, Y. Feldman

P-8 **Dielectric study of water in partially crystallized poly (ethylene glycol)-water mixtures**
M. Miyara, I. Takashima, K. Sasaki, R. Kita, N. Shinyashiki, S. Yagihara

P-9 **Dynamic behaviors of aqueous solutions restricted with the volume phase transition of poly(acryl amide) gels**
H. Saito, Rio Kita, N. Shinyashiki, S. Yagihara, M. Fukuzaki, M. Tokita

P-10 **Dielectric Study of the slow dynamics of proteins embedded in bioprotectant glassy matrices**
M. Pachetti, A. Paciaroni, A. Spepi, S. Capaccioli

Sessions S02: Polymer Dynamics

P-11 **Electrical properties of lithium ferrite / poly(lactic acid) composites**
S. Soreto Teixeira, M.P.F. Graça, N. Gama, A. Barros-Timmons, T. Cordeiro, M. Dionísio, L.C. Costa

P-12 **Complex dynamics of a fluorinated vinylidene cyanide copolymer highlighted by dielectric relaxation spectroscopy**
V. Castelvetro, S. Capaccioli, M. Raihane, A. Salima

P-13 **Thermoresponsive behavior of PNIPAM- and PMDEGA-based copolymers: comparative investigation**
D. Aravopoulou, M. Souli, K. Kyriakos, A. Miasnikova, A. Laschewsky, C.M. Papadakis, A. Kyritsis

P-14 **Dielectric and calorimetric studies on poly(lauryl acrylate)-b-poly(N-isopropyl acrylamide) block copolymers**
O. Vassiliadou, S. Kripotou, A. Skandalis, S. Pispas, A. Kyritsis

Session S03: Terahertz Spectroscopy

P-15 **Broadband Dielectric Spectrocopy on H_2O, D_2O, and $H_2{}^{18}O$, and Theoretical Calculations on the THz Spectral Component**
M. Nakatsuka, T. Nara, M. Okuda, N. Yamamoto, F. Zhang, K. Ohta, H. Shirota, S. Saito, K. Tominaga

P-16 **THz properties of BST bulk and film samples**
M. G. Banciu, L. Nedelcu

P-17 **Microwave dielectric characterization up to 1200 °C**
G. Annino, A. Cintio, A. Lazzeri

P-18 **Terahertz dielectric properties of Mg- and Zn-based silicate ceramics**
L. Nedelcu, C.D. Geambasu, M.G. Banciu, A. Iwamae, T. Furuya, M. Tani

Session S04: Broadband Dielectric Studies of Phase Transitions and Dynamics in Amorphous, Partially Ordered and Ordered Systems (Liquid and Plastic Crystals, Ferroelectrics, Ceramics, Pharmaceuticals, etc.)

P-19 **Intrinsic and extrinsic contributions in $(Ba,Sr)TiO_3$ ferroelectric**

ceramics studied by broad-band dielectric spectroscopy
L. Nedelcu, L. Trupina, C.P. Ganea, G.D. Geambasu, M.G. Banciu

P-20 **Centrosymmetric tetragonal B-site doped calcium copper titanate and its dielectric tunability**
N. Barman, S. Tripathi, N. Ravishankar, K. B. R Varma

P-21 **Dielectric relaxation in textured ferroelectric vinylidene fluoride copolymers with different morphology**
V.V. Kochervinskii, I.A. Malyshkina, S.A. Bedin, V.V. Volkov

P-22 **Electric and magnetic properties of Fe_2O_3--SiO_2--PbO glass manufacturing by traditional melt-quenching method and twin rollers fast-cooling method.**
A. Lenarciak, P. Kupracz, J. Strychalska, J. Karczewski, M. Gazda, R.J. Barczyński

P-23 **Interplay between the long range static ordering and dynamical heterogeneities determining the dynamics of the plastic crystal and ordinary liquid phases of the same material**
O. Madejczyk, E. Kaminska, K. Jurkiewicz, M. Tarnacka, K. Kaminski, A. Burian, M. Paluch

P-24 **Reorientational Dynamics in 1-F-adamantane**
B. Ben Hassine, M. Romanini, Ph. Negrier, M. Barrio, R. Macovez, D. Mondieig, A. Kallel, J.L. Tamarit

P-25 **Volume phase transition in thermo-responsive hydrogels as seen by dynamical mechanical analysis, dielectric spectroscopy and complementary techniques**
M. Kozanecki, M. Pastorczak, L. Okrasa, M. Olejniczak, K. Koynov, S. Kadlubowski

P-26 **Molecular dynamics of S-ibuprofen sodium salt in solid, solution and hydrogel states.**
L. Okrasa, M. Kozanecki

P-27 **The implication of various molecular interactions on dielectric behavior of cimetidine base and cimetidine hydrochloride**
M. Rams-Baron, Z. Wojnarowska, A. Jędrzejowska, M. Paluch

P-28 **The effect of temperature and pressure changes on the crystallization kinetics of fenofibrate**

G. Szklarz, K. Adrjanowicz, J. Knapik, K. Jurkiewicz, M. Paluch

P-29 **Effect of Polymer Molecular Weight and Concentration on Crystallization Behavior of Indomethacin-PVP Amorphous Solid Dispersions: Role of drug-polymer interaction and viscosity**
S. Mohapatra, P. Mistry, S. Samanta, R. Suryanarayanan

WEDNESDAY, 16:40 – 17:40

Session S05: Broadband Dielectric Studies of Phase Transitions and Dynamics in Amorphous, Partially Ordered and Ordered Systems (Liquid and Plastic Crystals, Ferroelectrics, Ceramics, Pharmaceuticals, etc.)

P-30 **Absence of correlation of fragility with dynamics and thermodynamics properties in binary mixtures of glass-formers**
K. Kessairi, S. Capaccioli, M. Bertoldo, V. Castelvetro, K.L. Ngai

P-31 **Electro-Rheological Effects in Glass-Forming Liquids: Does Entropy Control the Relaxation Time?**
S. Samanta, R. Richert

P-32 **High pressure dielectric studies on the plastic crystal, 1,6-anhydro-D-glucose and strongly H-bonded liquid, D-glucose**
E. Kaminska, M. Tarnacka, K. Jurkiewicz, K. Kaminski, M. Paluch

P-33 **Pressure dependence of Johari-Goldstein β-relaxation in 1-methylindole**
S. Valenti, S. Capaccioli, L.M. Wang, W. Tu, K.L. Ngai

Session S07: Investigation of Interfacial Phenomena and Confinement Effects

P-34 **Modeling of the dielectric and relaxation properties of nanostructured metal-containing films**
M.A. Kozhushner, V.L. Bodneva, O.J. Ilegbusi, L.I. Trakhtenberg

P-35 **Extracting material net properties of monomolecular coverages from BDS measurements with nano-structured electrode arrangements**

M. Tress, N. Neubauer, R. Winkler, P. Uhlmann, E.U. Mapesa, M. Reiche, F. Kremer

P-36 **Study of the dielectric properties of nanofluids using impedance spectroscopy**
B. Melo, M. A. Fonseca, B. Abreu, M. S. A. Oliveira, L. C. Costa

P-37 **Using compatibilization to tune dielectric properties resulting from conductivity mediated polarization at polymer-polymer, polymer-particle and polymer with particle-electrode**
A. Bharati, R. Cardinaels, M. Wübbenhorst, P. Moldenaers

P-38 **Study of the interfacial polarisation in SiO2/ Si bi-layer strucrure by dielectric spectroscopy**
H. Hammami

P-39 **Dielectric and conductivity studies of Polypyridinium triflate with carbon nanotubes**
I. Malyshkina, R. Pichugov, E. Makhaeva

P-40 **DSC, Optical and dielectric properties of polyvinyl alcohol/ cellulose nanocomposites**
N. Ghorbel, A. Kallel, S. Boufi

P-41 **Dielectric Properties measurements in large frequency and temperature ranges of natural rubber-cellulose nanocomposites**
N. Ghorbel, F. Agrebi, A. Kallel

P-42 **Structure and Dynamics of 2,3,6,7,10,11 hexakis[hexyloxy] triphenylene (HAT6) in Nanoporous Anodic Aluminum Oxide Membranes**
A. Yildirim, K. Sentker, P. Huber, A. Schönhals

P-43 **Dielectric investigations on carbon nanomembranes**
S. Madkour, P. Penner, X. Zhang, A. Gölzhäuser, A. Schönhals

P-44 **Effect of the fluid flow on the distribution of carbon nanotubes during the injection moulding of polymer nanocomposites**
J.F. Blanco-Villalba, R. Valente, D. Vlasveld, I. Mikonsaari, C. Hübner

P-45 **Molecular Dynamics of PMPS in uniaxial Pores of varying nanometric Diameter (5-10 nm)**
P. Prinz, F. Frenzel, F. Kremer

P-46 **Effect of architecture on polymer crystallization and dynamics under AAO confinement**
Y. Yao, T. Sakai, M. Steinhart, H.J. Butt, G. Floudas

P-47 **Dielectric investigations of attograms and zeptograms of matter**
A. Houachtia, G. Boiteux, J.-F. Gerard, A. Serghei

P-48 **Electrical and dielectric properties of composite materials: the role of morphology, volume fraction, form factor, orientation and presence of interphases**
M. Samet, A. Kallel, G. Boiteux, A. Serghei

Session S09: Broadband Dielectric Spectroscopy Applied to Life Science

P-49 **Evidence of proton wires in biomolecules by dielectric spectroscopy**
Y. J. P. Carreón, H. Mercado-Uribe

P-50 **Dielectric Spectroscopy of Biological Materials**
K.A. Motovilov, M. Savinov, A.A. Pronin, V. Grinenko, E.S. Zhukova, Z. Gagkaeva, K.V. Sidoruk, T.A. Voeikova, P.Y. Brazilovich, A.K. Grebenko, V.I. Torgashev, P. Bednyakov, M. Dressel, B.P. Gorshunov

Session S10: Charge Transport and Relaxation

P-51 **Mixed ion-polaron transport in ZnO-WO_3-P_2O_5 glasses containing Na_2O and Li_2O**
A. Šantić, J. Nikolić, D. Pajić, J.e Dragović, P. Mošner, L. Koudelka, A. Moguš-Milanković

P-52 **Enhanced photoluminescence and dielectric permittivity in Cr doped ZnS nanoparticles**
S. Virpal, J. Kumar, R. Thangaraj, S. Sharma, R.C. Singh

P-53 **Study of conduction mechanisms and dielectric properties of ZnO/MgO solid composites**
O. Hafef, M. Megdich, A. Matoussi

P-54 **New insight into ion transport through the dynamic modulus studies**
A. Jędrzejowska, K. Koperwas, M. Paluch

P-55 **Self-diffusion and Li+-ion conduction in succinonitrile-based plastic-crystalline electrolytes**

M. Zachariah, M. Romanini, P. Tripathi, M. Barrio, J.L. Tamarit, R. Macovez

P-56 **Large polaron conductivity in manganese borosilicate glass**
P. Kupracz, J. Karczewski, A. Lenarciak, M. Łapiński, M. Prześniak-Welenc, N. A. Szreder, R. J. Barczyński

P-57 **Conductivity in nematic liquid crystals: Nematic order, ionic concentrations and mobilities**
M. Kraska, M. Engel, A. Goetz, G. Bernatz, B. Stuehn

P-58 **Elucidating the effect of affinity and association on ion transport in polymeric desalination membranes using electrochemical impedance spectroscopy**
N. Fridman-Bishop, V. Freger

P-59 **Boundary conditions at electrode - ionic liquid interface for dielectric spectroscopy measurements**
C.P. Ganea, M.G. Banciu

P-60 **How Is Charge Transport Different in Ionic Liquids? : The Role of High Pressure**
B. Blanchard, S.N. Tripathy, Z. Wojnarowska, M. Paluch

P-61 **Structure and electrical properties of segregated polymer composites**
O. Maruzhenko, Ye. Mamunya, G. Boiteux, A. Serghei, S. Pusz, U. Szeluga, B. Kumanek

P-62 **Solid polymer electrolyte composites based on epoxy oligomer and lithium perchlorate salt: thermal characteristics, ion-conductivity and permittivity**
L.K. Matkovska, M.V. Iurzhenko, Ye.P. Mamunya, O.K. Matkovska, G. Boiteux, A. Serghei

Late submissions

P-63 **Towards Microvolume Dielectric Spectroscopy of Biomolecules**
Daniel Havelka, Ondrej Krivosudský, Michal Cifra

Oral contributions

Dielectric susceptibility of Liquid water: microscopic insights from neutron scattering and MD-simulations

J. Colmenero

Materials Physics Center (CSIC-UPV/EHU)); University of the Basque Country, San Sebastián, Spain

Water dynamics has paramount importance in many areas of research and industrial applications. One of the main techniques used from the early times to investigate water dynamics is dielectric spectroscopy (DS). Thanks to the development of the tera-herz (THz) techniques it was recently possible to fill the gap between dipolar relaxation and intermolecular streatching vibrations at ≈5THz and to have a full picture of the dielectric permitivity $\varepsilon^*(\omega)$ of liqid water in a broad frequency (ω) range. These results reveale that in addition to the main dipolar relaxation –the so-called Debye peak due to collective dipolar relaxation- additional low amplitude processes need to be invoked for describing the high-frequency part of the spectrum. The nature of these high frequency processes is still a matter of debate. Moreover, the interpretation of the molecular motions involved in the different dielectric processes is very unclear, mainly because DS is a 'macroscopic' technique, which follows the fluctuations of the total dipole moment of the system without spatial resolution. Interestingly, the relevant frequency range for the dielectric response of liquid water can also be covered by neutron scattering (NS), a tehnique delivering microscopic information with spatial/time resolution. Moreover, by measuring deuterated water (D_2O) samples, NS reveals the dynamic structure factor ($S(Q,\omega)$), with Q the wavevector, i.e., it allows following the actual structural relaxation.

Although the synergetic combination of NS and DS has proven to be a powerful tool in different but likely related problems as, for instance, dynamics in glass forming polymers, this methodology has never been explored for water dynamics. In this work, we have considered DS data together with coherent and incoherent NS data of water at room temperature. The NS data were analyzed in terms of the corresponding susceptibility –a less conventional way that allows distinguishing better the different processes involved as well as the comparison with spectroscopy DS data. We have also carried out molecular dynamics (MD) simulations in order to unveil the microscopic origin of the different processes involved. We achieve a unified description of both NS and DS susceptibilities, which allows clarifying the nature of the different relaxation processes, the molecular motions involved in the DS spectra and their impact on the structural α-relaxation directly monitored by $S(Q_{max},\omega)$, where Q_{max} is the Q-value of the maximum of S(Q). These results also open a new way of approaching dynamics of water under different conditions (supercooled, confined, etc.) and that of other H-bonded liquids.

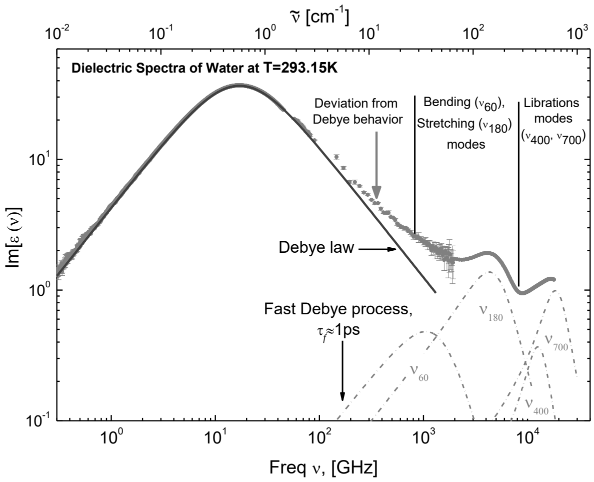
The mechanism of the dielectric relaxation in water

Ivan Popov[1,2], Paul Ben Ishai[1], Airat Khamzin[2] and Yuri Feldman[1]

[1]The Hebrew University of Jerusalem, Department of Applied Physics, Edmond J. Safra Campus, Givat Ram, Jerusalem 91904, Israel

[2]Kazan Federal University, Institute of Physics, 420008, Kremlevskaya str.18, Kazan, Tatarstan, Russia

Although relating to the same system, the interpretations of the water spectra from Raman and Dielectric spectroscopy present independent pictures of the nature of water. We show that in the overlap region of the two methods it is possible to combine these views into a coherent concept of what drives the dynamic features of water. In this work, we develop the idea that the dielectric relaxation in water is driven by the migration of defects through the H-bond network. The normal diffusion of the defects leads to a Debye-like peak in the lower frequencies. The deviation from the Debye law in the higher sub-THz frequencies is traced to a global fluctuation of the same H-bond network, clearly evident in the Raman Spectra [1]. By incorporating these two views, a mathematical formalism is presented that can aptly explicate the dielectric spectra of liquid water, without involving the secondary fast Debye process [2].



Besides the dynamical properties, we found the relationship between the static dielectric permittivity and the correlation length between water molecules. It was shown that this length is limited to the defect lifetime and can be associated with the minimal size of a water cluster. In turn, this correlation length allowed us to calculate the number of closest neighbors of a water molecule. Taking this and Kirkwood's formula into account, we derived a more accurate equation for the temperature dependence of the static dielectric permittivity, which was in good agreement with the experimental data.

[1] Walrafen, G. E. et al. J Phys Chem-Us 93, 2909-2917 (1989).
[2] Buchner, R. et al. Chem Phys Lett 306, 57-63 (1999).

Mixing effects on the structure and dynamics of monohydroxy alcohols

S. Peter Bierwirth, Thomas Büning, Jonas Lueg, Christian Sternemann, Catalin Gainaru, Metin Tolan, Roland Böhmer

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The dipolar response of monohydroxy alcohols attracted scientific interest for more than a century [1] and the understanding of their Debye process has a long and not always straightforward history. It is clear though that in these liquids the formation of hydrogen-bonded suprastructures has profound effects on their structure and dynamics [2]. Due to a typically very good resistance against crystallization, viscous monohydroxy alcohols can be studied continuously over wide temperature ranges, unlike the situation encountered for supercooled water [3]. Using a combination of broadband dielectric spectroscopy, shear rheology, and x-ray diffraction we report on interesting effects in mixtures of isomeric octanols with alkyl halides.

Work supported by the Deutsche Forschungsgemeinschaft (under Grant Nos. BO1301/8-1 and BO1301/8-2), the BMBF (Project 05K13PE2 within FSP-302), and MERCUR (AN-2014-0036).

[1] P. Debije, Zur Theorie der anomalen Dispersion im Gebiete der langwelligen elektrischen Strahlung, Verh. Dtsch. Phys. Ges. **15**, 777 (1913)

[2] R. Böhmer, C. Gainaru, R. Richert, Structure and dynamics of monohydroxy alcohols – milestones towards their microscopic understanding, 100 years after Debye, Phys. Rep. **545**, 125 (2014); S. Bauer, K. Moch, P. Münzner, S. Schildmann, C. Gainaru, R. Böhmer, Mixed Debye-type liquids studied by dielectric, shear mechanical, nuclear magnetic resonance, and near-infrared spectroscopy, *J. Non-Cryst. Solids* **407**, 384 (2015)

[3] E.g., K. Amann-Winkel, R. Böhmer, C. Gainaru, F. Fujara, B. Geil, T. Loerting, Water's controversial glass transitions, Rev. Mod. Phys. **88**, 011002 (2016); See also the collection of articles in the special issue on "Water—The Most Anomalous Liquid" published in Chem. Rev. **116**, Issue 13 (2016)

Are there possibilities to learn something new from pressure studies of primary alcohols?

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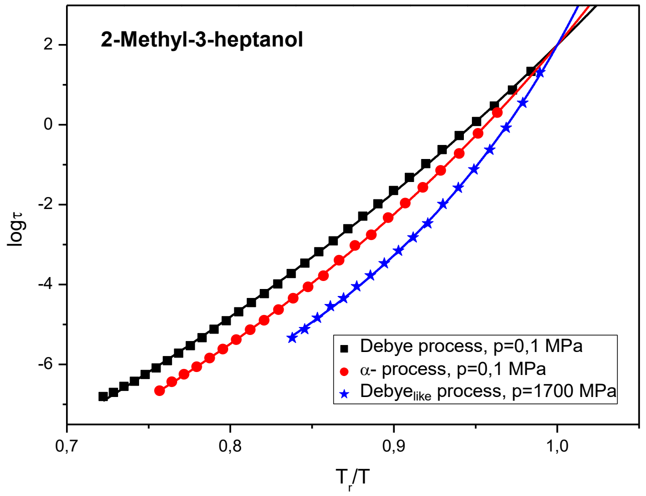
During last few years, a series of investigations performed on monohydroxy alcohols, reflect the importance of these materials in studies over understanding properties of hydrogen bonded structures. Existence in the dielectric and mechanical spectra of so-called Debye process, is directly related to the H-bonded supramolecular architecture, enabled insight into features of these structures. Most the studies have been carried out only at ambient pressure but few of them, also conducted at elevated pressure showing unique changes of the dynamics of the associated structures during pressurization. Unambiguosly, the high density conditions are very important for molecular dynamics of supramolecular structures that are responsible for unique features of the alcohols. However, because of similar changes in the properties at high pressure conditions were observed in different alcohols, one may expect that nothing new can be discovered during further investigations of this family of materials. Is this expectation reasonable?

In this presentation, we pose key answers to these question based on results from studies on a series of primary alcohols, previously not tested. These results, collected at various p-T conditions, provide new observations about features of the alcohols e.g. dramatic increase of the *steepenes index* of the Debye process at high pressure conditions above the value noticed for the structural relaxation at ambient pressure. Moreover, the previously concealed features suggest that we are still far from well understanding of molecular origins, responsible for unique properties of the alcohols and, more generally, the associated liquids.



Intra- and Intermolecular Contributions to the Dynamics of Polymer Melts

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The cooperative dynamics generalized Langevin equation is a microscopic, force-level, theory of the dynamics of a group of interacting polymers in a dynamically heterogeneous environment. The theory is fundamental because is derived by projecting the Liouville dynamics onto the coordinates of the slow variables. The theory is general, as it conveniently covers dynamics from the unentangled to the entangled regimes. It provides a microscopic picture of the dynamics, because it clearly identifies, for example, intra and intermolecular contributions to time correlation functions, such as P1(t) and P2(t), that are relevant for dielectric relaxation measurements.

Diffusion in Complex Polymer Systems Modeled with Cooperative Dynamics and The Dedicated Simulator

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Modeling of diffusion processes in complex polymer systems is a challenging task and nowadays is becoming very important issue. Extremely different diffusion relaxation time scales for solvent and polymer units makes this problem even more interesting. Only a few stochastic methods exist were polymer systems can be studied as a dense media with satisfied excluded volume condition. One of them was first published by Prof. T. Pakula [1] – the Dynamic Lattice Liquid (DLL) model. It is based on the assumption that liquid molecular system can be considered as an assembly of structureless beads representing atoms or groups of atoms. Algorithm based on this model assumes that diffusion steps of molecules are realized as a cooperative motion.

The DLL algorithm was already successfully applied for various non-equilibrium physical and chemical problems in polymer science, like polymer chains dynamics [2,3], gelation process [4] and polymer stars formation [5]. Recently, this model was also used for modeling of solvent dynamics in the neighborhood of brushed-like polymer chains [6]. The influence of both polymer chain length and concentration on the mobility of solvent molecules in polymer solutions was studied. Two majorly different solvent states with differing mobilities were distinguished. The first one, with high molecular mobility independent of polymer concentration, corresponds to bulk solvent in real systems. The second state relates to so called bound solvent.

The unique dynamic properties and parallel nature of DLL gave basis for the idea of massively-parallel simulator – ARUZ (stands for Analyzer of Real Complex Systems). ARUZ consists of a huge number of FPGA circuits (configurable devices) implemented in one structure interconnected in dense three-dimensional network. ARUZ is installed in Technopark Lodz in Poland and enables studies of dynamic processes and phenomena of complex molecules or macromolecules. It enables simulations of three dimensional systems containing theoretically up to few millions of elements (united atoms) in relatively long time scales.

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Heterogeneous dynamics and plasticity of a stretched polymer glass studied by dielectric spectroscopy

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We study the dielectric relaxation of polycarbonate (PC) at room temperature under imposed strain rate $d\gamma/dt$, above the yield stress and up to 13 % strain. We find that the dielectric response of stretched PC behaves as if it was heated up at a temperature just below its glass transition temperature Tg = 423 K for PC. Indeed, in the frequency range of our experiment 0.01 Hz and 1000 Hz, the dielectric response of the stretched PC at room temperature superimposes to the dielectric response of PC at a temperature Ta ($d\gamma/dt$)<Tg, which is a function of strain rate. Specifically we observe that at Ta the dominant relaxation time t_a(Ta) of PC at rest is related to $d\gamma/dt$ in such a way that t_a(Ta) = 1/ ($d\gamma/dt$) at and beyond the yield point. In our experiment 10^5 s^{-1} < $d\gamma/dt$ <10^{-3} s^{-1}, the temperature shifts Tg-Ta are of a few K. The mechanical rejuvenation modifies the dielectric response at frequencies smaller than 10 Hz, whereas for higher frequencies the spectrum is only slightly modified.

Structure-dynamics relationship in biobased polyesters of 1,3-propanediol as revealed by dielectric spectroscopy

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Due to the limited availability of fossil sources and their price fluctuations, the current interest of both academic and industrial communities is nowaday focused on the development of polymeric materials from renewable resources.

Among the so-called green chemicals, 2,5-furandicarboxylic acid displays a large potential as green monomer[1] for the synthesis of new polyesters able to replace the very important thermoplastic polymers based on petroleum-derived terephthalic acid, from which differ for the substitution of the benzene ring with a furanic one.

1,4-cyclohexanedicarboxylic acid is also a biobased monomer[2], whose polyesters proved to be biodegradable[3]. The presence of an aliphatic ring permits conformational isomery, not possible for the aromatic ring, which strongly influences the final properties[3]. Lastly, 1,3-propanediol can be also obtained by renewable feedstocks[4].

Taking into account this scenario, poly(propylene 2,5-furanoate) (PPF) and poly(propylene 1,4-cyclohexanedicarboxylate) (PPCE) have been synthesized and the structure-dynamics relationship has been investigated by means of dielectric loss spectroscopy, focusing the attention on sub-glass relaxations. The two new biobased polyesters have been then compared with the well-known poly(propylene terephthalate) polyester (PPT) previously investigated[5], in order to evaluate the effect of substitution of the aromatic ring of PPT with the aliphatic ring of PPCE, on one side, and with the furanic ring of PPF, on the other side. The corresponding polyesters of neopentyl glycol have been also prepared and taken into consideration. In fact, as previously pointed out in the case of terephthalic-based polyesters[5], the substitution of the two hydrogen atoms of the methylene group in β position with respect the ester oxygen with methyl groups renders the mcromolecular chains stiffer and consequently significantly impacts on sample dynamics.

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Insights into the Relaxations of Hydroxypropyl Methylcellulose via Broadband Dielectric Spectroscopy

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Hydroxypropyl methylcellulose (HPMC) has several physical properties desirable for drug delivery, including water solubility and low crystallinity. Unfortunately it has a glass transition temperature near its degradation temperature, which makes compounding, extrusion, and pellet molding difficult. Commercial HPMC is a unique polymer, formed from natural cellulose, and therefore has no long chain branching. Also, due to its glycosidic backbone, it has a persistence length several times larger than most polymers. It is perhaps related to some or all of these physical properties that the glass transition of HPMC is difficult to measure with differential scanning calorimetry and broadband dielectric spectroscopy. In the present study we measured several different relaxations in a novel grade of HPMC with a glass transition low enough to allow it to be melt processed. The ability to understand and potentially tailor the glass transition of HPMC has positive implications for the pharmaceutical industry.

Interaction of high-intense femtosecond radiation with gas medium and gas cluster beams: generation of the high intesity THz and X-ray radiation and their applications.

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Interactions of laser radiation with gas cluster targets have been investigated in the past two decades. Cluster jet, obtained by the adiabatic condensation of gas flow, has pronounced nonlinear optical properties and combines the advantages of solid-state and gas target. Cluster inherits high local density and this implies high value of nonlinear response: generation of X-ray radiation, generation of optical harmonics, self-focusing, Stimulated Raman Scattering.

In some recent publications, intense THz generation in cluster beam excited by ultrashort laser pulses was reported. At the present moment there is no clear theoretical interpretation of the experimental results and complete understanding of the mechanism of low-frequency emission in cluster plasma. It seems reasonable to carry out further study of terahertz generation in a clustered plasma, and examine this process in both ways: as a fundamental issue of laser-matter interaction on the way to solving a problem of the dynamics of laser-cluster interaction, and as a practical goal of obtaining an effective source of pulsed THz radiation. In addition, there is possible to apply two-color excitation scheme, which has been successfully used in the past to increase the efficiency of the optical to terahertz conversion in laser-induced plasma of gas media. Two-color scheme allows to increase THz yield by 2…3 orders of magnitude and nowadays this scheme is widely used for THz generation in gaseous media.

In this paper we present the results of experimental and theoretical studies of generation of terahertz emission in the laser-induced clustered plasma. We have performed experiments using both single-color and two-color excitation schemes. Simultaneously with the control of terahertz emission of clustered plasma we measured the power of accompanying X-ray radiation, which is an important source of information about the processes that occur in a cluster plasma. In the theoretical section we made an attempt to explain the experimental results.

The role of the JG β-Relaxation for the physical stability of organic molecular glasses – new insights from THz-TDS measurements and molecular dynamics simulations

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Terahertz time-domain spectroscopy (THz-TDS) is a non-contact measurement technique that can be used to extend the experimentally accessible range for the measurement of dielectric relaxations from frequencies of about 100 GHz to 3 THz and beyond. We have recently reported a series of experiments where we measured the dielectric losses at terahertz frequencies using THz-TDS over a wide range of temperatures from 80 K to well above the T_g for a range of organic molecular glasses.[1] At temperatures below the glass transition of the primary relaxation we found that the losses at terahertz frequencies responded to changes in temperature as was expected for the Johari-Goldstein (JG) β process, albeit at much higher frequencies. Based on our results we speculated that we had observed the T_g of the JG β-relaxation using THz-TDS. Capaccioli, Ngai and coworkers convincingly argued that our observation of these processes at terahertz frequencies could be explained by the coupling between the caged molecule dynamics and the JG β-relaxation and that this phenomenon can also be picked up by other high frequency scattering techniques.[2-4] We investigated the relationship between the physical stability of a range of drug molecules in the amorphous state and the strength of the JG β process as measured indirectly by THz-TDS.[5] We found clear evidence of the fundamental importance of the JG β-relaxation during the crystallisation process and there was a clear correlation between the strength of the JG β-relaxation and the time to crystallisation under ambient conditions.

By combining experimental results with theoretical simulations we aim to better understand the molecular dynamics of molecular glasses. However, the disordered nature of such materials makes them ill-suited for common solid-state density functional theory (DFT) methods, where periodic boundary conditions would require extremely large unit cells to effectively reproduce the physical system. Moreover, static DFT calculations are unable to take temperature effects into considerationYet, new advancements in ab initio molecular dynamics, a fully first-principles approach, enable the study of amorphous dynamics in a relatively straightforward fashion. We show first results in exploring the temperautre effects on both crystalline and amorphous materials, specifically the changes in the infrared spectra and compare the results to experimental observations.

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Broadband Dielectric Spectrocopy from MHz to THz on Proteins; Comparison between Globular Proteins and Membrane Proteins

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Recenlty, we reproted a dielectric spectral study of lysozyme in a solid state to show the effects of hydration and thermal excitation on the low-frequency dynamics of protein.[1] Dielectric measurements were performed under changing hydration conditions at room temperature in the frequency region of 0.5 GHz to 1.8 THz. We also studied the temperature dependence (83 K to 293 K) of the complex dielectric spectra in the THz frequency region (0.3 THz to 1.8 THz). To reproduce the spectra, we found that two relaxational modes and two underdamped modes are necessary in the model function. At room temperature, the two relaxational modes have relaxation times of ~20 ps and ~100 ps. The faster component has a major spectral intensity and is suggested to be due to coupled water-protein motion. We observed a protein-dynamical-transiton-like behavior in the temperature dependence of the absorption spectra of protein in the THz region. From our broadband measurements, we conclude that the increase in the spectral intensities in the THz region at approximately 200 K is due to a spectral blue-shift of the relaxational mode. In this report, we present results of the broadband dielectric measurements on bacteriorhodopsin, one of the membrane proteins, to discuss the effects of hydration and thermal excitation on its low-frequency dynamics. We especially focus on the 'temperature hysteresis' of the spectral intesity, which is related to the supercooled water around the protein. We compare this hysteresis between the globular proteins and bacteriorhodopsin.[2]

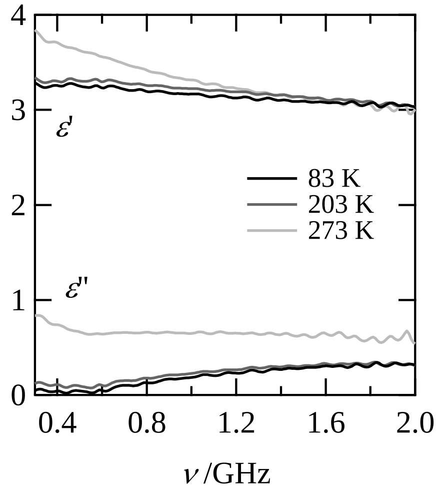

Figure 1. Complex dielectric spectra of bacterio-rhodopsin with h = 0.52. The definition of h is the gram amout of water per one gram of protein.

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Boson Peak and Fast Dynamics of Glassy Matter

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The dielectric absorption spectra of many glass forming materials at terahertz frequencies are dominated by an excitation that seems to occur quite universally in disordered systems but whose microscopic origin is still a matter of debate. This interesting feature, which is located in between the classical spectral regions of dielectric and infrared spectroscopy, can also be observed with other techniques such as inelastic neutron and light scattering as well as in calorimetric measurements, where it shows up as an excess term in the specific heat. Since its temperature dependence in the scattering experiments can be described by the Bose-Einstein statistics, it is sometimes referred to as 'boson peak'.

Employing temperature-dependent terahertz time-domain and Fourier-transform far infrared spectroscopy, dielectric spectra of several liquids as well as solid disordered samples in the frequency range of 0.1 – 20 THz could be obtained. Thereby the spectral shape of their boson peak was resolved with hitherto unrivalled precision.

We mainly focused on the so-called ‘plastic crystals’, which consist of dipolar molecules that form a regular crystal lattice with respect to their centers of mass but are rotationally disordered. Due to their translational symmetry, they can quite easily be treated theoretically and therefore are often considered as model systems for structural glass formers. From an experimental point of view, it is a big advantage that most of the plastic crystals can be prepared in several different phases, depending on the cooling rate. By following the evolution of the boson peak under temperature variation and at phase transitions and by comparing it to the results for canonical glass formers, valuable hints to unravel its true nature are obtained.

Terahertz spectroscopy of incipient ferroelectric state of nanoconfined water molecules

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Though having large molecular electric dipole moment (1.85 D), liquid water does not reveal any *dipolar* order, because the intermolecular dipole-dipole interactions are suppressed by the hydrogen bonds. On the other hand, computer simulations demonstrate possibilities of ferroelectric orderings of H_2O molecules that are *nanoconfined* within carbon nanotubes, fullerenes or spread over two-dimensional surfaces. This kind of confined-water ferroelectricity is considered to play a significant role in various processes in nature, including living organisms. Until now, however, no clear and incontrovertible *experimental* evidences have been obtained for any kind of H_2O dipoles ordered state. We have studied the dielectric response of a system of water molecules localized within structural channels formed by ions of the beryl crystal lattice. The distance between the pores that form the channels and host water molecules is large enough (5 Å to 10 Å) to weaken the hydrogen bonds (effective interaction range 1-2 Å) but not too large to keep the dipole-dipole coupling effective (effective interaction range 10-100 Å). Using broad-band terahertz and radio-frequency spectroscopies, we have detected firm signatures of dipolar ordering within the subsystem of H_2O molecules located within the crystalline matrix. At terahertz frequencies, we detect a ferroelectric soft mode whose frequency obeys the Cochran temperature behavior and whose dielectric contribution leads to the Curie-Weiss temperature dependence of the quasi-static dielectric constant. Below 10 K, we observe saturation of the dielectric constant and of the soft-mode parameters that indicate incipient ferroelectricity of the water molecules ensemble. We describe our results within the framework of a mean-field microscopic model that considers rotational and librational motions of interacting water molecular dipoles in a six-well potential. In addition, at infrared frequencies highly anisotropic absorption bands are observed and assigned to librational and translational vibrations of nanocaged water molecules.

Dielectric relaxation in self-assembled diphenylalanine nanotubes.

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Self-assembled diphenilalanine nanotubes (FF NT) form their hexagonal structure as a result of water reaction with L-Phe-L-Phe molecules. The hexagonal structural units self organized by two covalently linked phenylalanine (FF), which is a key structural motive of β-amiloid polypeptide of Alzheimer's disease. The discovery of a number of physical properties such as second harmonic genaration, pyroelectric and piezoelectric effects, along with their biocompatibility, make them attractive targets not only for applications but also for fundamental investigation.

In this work we study dielectric properties of FF NTs in a wide temperature and frequency range and revealed a squence of phase transitions at 170K, 200K, 230K and 300K. The dielectric relaxational modes related to each phase have been founded out. Two relaxation processes were observed at low temperatures. The fast mode of Arrhenius type, appearing at temperatures much lower than 170K was identified as motions of amino dipoles located in 6FF hexagonal rings. Relatively slow mode exibited non-Arrhenius evolution with temperature was ascribed to for supercooled confined water. The fragile-strong crossover was found to occur at 195K in FF NT.

The transition at 230K was identified as structural transformation from antipolar orthorombic to hexagonal symmetry ($D_{2h} \rightarrow D_{6h}$), as predicted in [1]. It was found that structural transformation at 230K is the rubicon of crucial changes of dielectric relaxational modes in FF NT. At T>230K unusual saddle-like evolution of relaxation times have been founded out in FF NT. The theoretical consideration of similar nonmonotonic relaxation of water in confined systems was given in [2]. In this phase, the distinction of FF NT is that the nonmonotonic relaxation behavior accompaned with additional cooperative mode related to motions of carboxile-water complexes. The conclusion is made regarding the polar properties of FF NT.

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Dynamics in translationally ordered solids

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We present the results of dielectric studies carried out, both as a function of temperature and pressure, on a number of translationally ordered molecular solids. The probed phases range from plastic crystals to solids with occupational orientational disorder, and from phases displaying molecular isomerism to layered materials. The aim is to investigate the impact of the degree of disorder and of the number of degrees of freedom on the characteristic properties of molecular relaxations. We find, surprisingly, that systems where the disorder is limited to a reduced number of molecular degrees of freedom exhibit in general a rich relaxation behavior, which is a priori unexpected. In particular:

- dynamic relaxations can be observed also in systems that are considered „ordered" from a crystallographic point of view;[1]
- in highly anisotropic solids, different cooperative relaxations arise, associated with different rotational molecular degrees of freedom, *e.g.* different axes of rotation;[2,3]
- such orientational relaxations follow a thermodynamic scaling behavior similar to that reported for van der Waals systems;[3]
- fixed-angle reorientations between indistinguishable initial and final states can be observed by dielectric spectroscopy;[4]
- there exist Johari-Goldstein precursor relaxations associated with cooperative large-angle reorientations;[1,4]
- in some plastic rotator phases, a Stokes-Einstein relation between self-diffusion and orientational dynamics is found to be valid.[5,6]

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Ionic and dipolar dynamics in binary plastic crystalline systems

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Solid-state electrolytes are seen as a promising way to overcome a number of problems in the design of new electrochemical energy-storage devices [1]. However, the development of a solid electrolyte with room temperature ionic conductivity comparable to that of a liquid electrolyte and mechanical properties of a solid is still in progress.

There is a whole class of materials naturally combining the properties of liquid and solid-state matter, namely the plastic crystals (PC). In PCs, below a certain transition temperature the centers of mass of the molecules form a regular crystalline lattice but they retain their orientational degree of freedom. When ions are added, various PC systems were shown to be relatively good ionic conductors. Especially for the succinonitrile (SN) PC-phase a remarkable high dc-conductivity at room-temperature was found [2]. It was suggested that the rotational molecular motion is responsible for the high ionic mobility. Very recently it was shown that adding a second component to this PC system leads to an increase of the ionic conductivity over several decades [3].

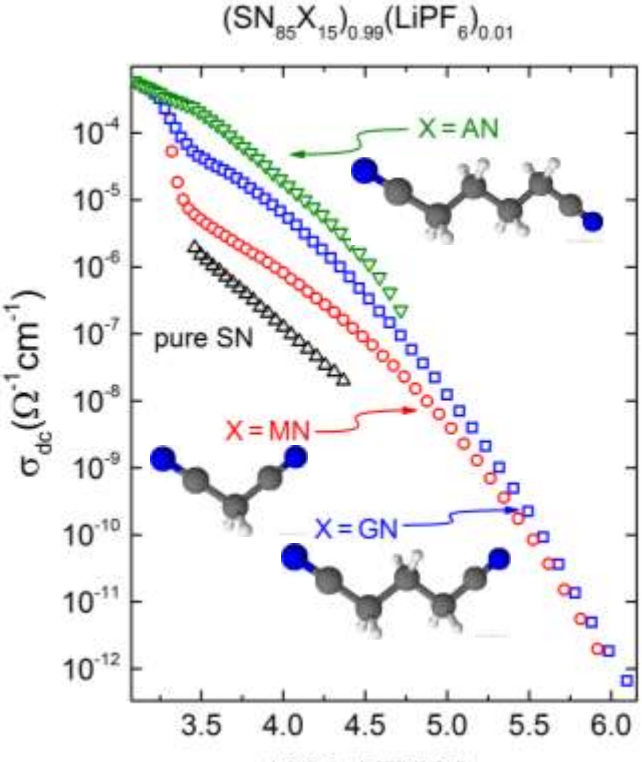

Fig. 1: Temperature-dependent conductivity of various binary SN-based PC-systems.

In the present work, we systematically vary this second component (Fig. 1). We provide a thorough investigation of the dielectric properties of these binary PC systems to understand the underlying dynamics causing the high ionic mobility.

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An unique secondary relaxation in the rigid glass forming molecular liquid of 1-methylindole

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Molecular liquids with very rigid structure like toluene usually show a resolved dielectric Johari-Goldstein (JG) secondary (β-) relaxation, which can be well explained by coupling model. Yet, such measurements for the rigid liquids are somehow limited. Here, we studied the dielectric relaxation in three glass-forming molecular liquids, 1-methylindole (1MID), 5H-5-Methyl-6,7-dihydrocyclopentapyrazine (MDCP), and Quinaldine (QN) by focusing on the secondary relaxation and its relation to the structural α-relaxation. All three glass-formers are rigid and more or less planar molecules with related chemical structures but have dipoles of different strengths at different locations. A strong and fast secondary relaxation is detected in the dielectric spectra of 1MID, while no resolved β-relaxation is observed in MDCP and QN. If the observed secondary relaxation in 1MID is identified with the JG β-relaxation, then apparently the relation between the α- and β-relaxation frequencies of 1MID is not in accord with the coupling model. The possibility of the violation of the prediction in 1MID as due to either the formation of hydrogen-bond induced clusters or the involvement of intramolecular degree of freedom is ruled out. The violation is explained by the secondary relaxation originating from the in-plane rotation of the dipole located on the plane of the rigid molecule, contributing to dielectric loss at higher frequencies and more intense than the JG β-relaxation generated by the out-of-plane rotation. Experimental evidence for the explanation is explored by the mixing experiments of the ploar 1MID with two glass forming liquids with weak polarity but higher or lower glass transition temperature, Tg, and the dielectric relaxation of 1MID in the two mixtures is found to have the same β-relaxation dynamics. MDCP has smaller dipole moment located in the plane of the molecule; however, presence of the change of curvature of dielectric loss at some frequency on the high-frequency flank of the α-relaxation reveals the JG β-relaxation in MDCP and which is in accord with the CM prediction. QN has as large an in-plane dipole moment as 1MID, and the absence of the resolved secondary relaxation is explained by the smaller coupling parameter than the latter in the framework of the CM.

Spatially Heterogeneous Nature of Secondary β-Relaxation

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Glass is abundant in *Mother Nature* and offers robust functional response to technology. Any liquid transforms to a glass when supercooled (or compressed) rapidly enough to avoid crystallization and employ many-body irreversible structural relaxation (α) process to explore the potential energy landscape of the system to attain equilibrium state that undergoes a kinetic arrest when α-relaxation time exceeds the observational time scales at about 100 s. The corresponding temperature is known as glass transition temperature, T_g. Below this temperature, the dynamic and thermodynamic properties of the system become strongly sensitive to thermal history and display temporal evolution. Moreover, the structure of glass is also not identical to the extrapolated locus of equilibrium liquid below T_g. As a result, we notice a relaxation of its structure, volume and enthalpy on geological timescale in the direction of extrapolated equilibrium values to attain the equilibrium state. Thus, it is virtually impossible for humans to understand the aspects of equilibrium glass and warrant a suitable probe. Note that below T_g, glassy materials show essential properties connecting the existence of the secondary (β) relaxations that manifest the principal source of dynamics. The perturbation in β-process is accommodated through dynamics, packing and disorder in the material.

In this presentation, we provide key answers to the above mentioned problems. As the structure and density in glassy state depend on its history which deforms the shape of the potential energy landscape, authors suggest a radical thermodynamic path to prepare a high density amorphous state of matter using high pressure which is anomalous to conventional supercooling approach. We found that glass prepared using these technique exhibit properties of conventional glasses annealed thousand years. In addition, we provide the impeccable experimental evidence of spatially heterogeneous nature of secondary β-relaxation and probe its properties to understand the various aspects of the equilibrium glass such as dynamics, packing and disorder. These features are expected to provide new horizons to glass preparation and functional response to pharmaceutical applications.

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Entropy-Enthalpy Compensation in Glass Formers

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Meyer-Neldel compensation or as it is more widely known Entropy-Enthalpy compensation has been noted in a wide variety of systems. It is an effect that indicates (at least in the common understaning relating to semiconductors) a certain amount of cooperative behavior, and provides a straightforward "scaling" mechanism for phenomena at differnt time scales. The foundations of the effect are not yet fully understood as there is no general, truly molecular, statistical mechanical explanation. Instead there are only many locally applicable theories, leading to some skepticism as to the true physical reality of the phenomena.

The appearance of this effect has been noted in various isolated instances in glass formers, but in these materials no comprehensive framework has yet been provided at all, in order to account for it. It was demonstrated on a wide scale in the Johari-Goldstein beta relaxation for a variety of very different materials. It shall be shown, that this same compensation behavior can be extended to the alpha process, in two ways. First in the viscosity high temperature data in the Arrhenius region of the relaxation. Second, in the broadband dielectric relaxation data of these same glass formers. Using a slight modification of the Adam-Gibbs formulation the analysis can be applied to the Vogel-Fulcher-Tammann equation, and effective parameters can be extracted from the non-Arrhenius behavior as well.

Conecting all three of these experimental findings and elucidating the connections and interplay between them provides a comprehensive explanation for the compensation effect in glass formers. Furthermore, it can be suggested that this may provide vital insight into the entropy-enthalpy compensation effect itself as well.

External dc bias field effects in the nonlinear ac stationary response of dipolar particles in a mean field potential

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External dc bias field effects on the nonlinear dielectric relaxation and dynamic Kerr effect of a system of permanent dipoles in a uniaxial mean field potential are studied via the rotational Brownian motion model postulated in terms of the infinite hierarchy of differential-recurrence equations for the statistical moments $f_n(t) = \langle P_n \rangle (t)$ (the expectation value of the Legendre polynomials P_n). By solving these equations, the nonlinear dielectric and Kerr effect ac stationary responses are evaluated for arbitrary dc field strength via perturbation theory in the ac field. Simple analytic equations based on the large separation of the time scales of the fast intrawell and slow overbarrier (interwell) relaxation processes are also derived.

Fifth-order susceptibility unveils the growth of thermodynamic amorphous order in glass-formers.

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Glasses are ubiquitous in daily life and technology. However, the microscopic mechanisms generating this state of matter are still controversially debated: glasses are considered either as merely hyper-viscous liquids or as resulting from a genuine thermodynamic phase transition towards a rigid state. We show that third and fifth order susceptibilities provide a definite answer to this longstanding controversy. Indeed, if an amorphous thermodynamic order is growing upon cooling, the fifth order response should be more anomalous in temperature and in frequency than the third order one. This is because each of the nonlinear responses is related to the size of amorphously ordered domains raised to some exponent; but the higher the order of the response, the larger the exponent.

Owing to the extreme smallness of nonlinear responses, we have performed high precision dielectric experiments in two independent setups, yielding consistent results. More precisely, we have measured the third- and fifth-order response respectively at the third and fifth harmonics for supercooled glycerol and propylene carbonate.

We find strong support for theories based upon thermodynamic amorphous order. Moreover, when lowering temperature, we find that the growing transient domains are compact, i.e. their fractal dimension $d_f=3$. The glass transition may thus represent a new class of critical phenomena, different from canonical second-order phase transitions for which $d_f<3$.

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Tuning the Entropy of Dielectrics by High DC Fields: Experiments and Models

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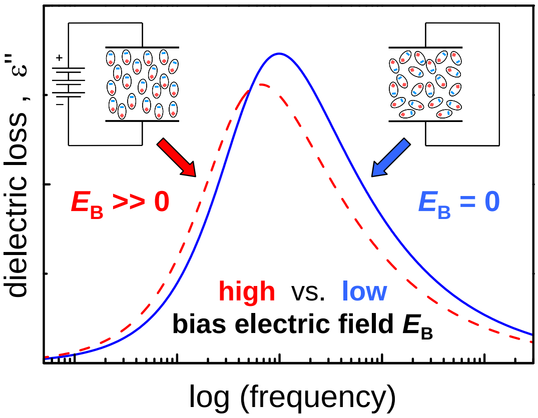
At sufficiently large electric fields, the permittivity becomes field dependent and higher order Fourier components of polarization appear [1]. Various sources of such non-linear dielectric effects exist: saturation that decreases $\Delta\varepsilon$, chemical effects that increase $\Delta\varepsilon$, energy absorption reducing τ_α, and the consequence of field induced entropy changes which lead to increasing τ_α [2].

The various origins of the non-linear effects can be discriminated by proper choices of the experimental protocols, namely high ac versus high dc fields, and by frequency range. On the basis of experimental techniques that facilitate time-resolved studies of how the system approaches equilibrium with the high field, it is demonstrated that the average structural recovery time is required to reach steady state [3], analogous to physical aging.

A relatively recent discovery is the electro-rheological effect of polar liquids, referring to a high dc bias field increasing the primary structural relaxation time and viscosity. In a dielectric relaxation experiment, this feature is observed as a field induced shift of the entire loss peak, $\varepsilon''(\omega)$, to lower frequencies, relative to the low field case, as depicted schematically in Fig. 1. It is found that the magnitude of this shift is largely a matter of the field induced change of the thermodynamic entropy, $\Delta_E S = \frac{1}{2}\varepsilon_0\, \upsilon(\partial\varepsilon_s/\partial T)\, E^2$.



Non-linear features can also be detected via the occurrence of higher order Fourier components of polarization, e.g., a third harmonic susceptibility. This third harmonic signal, $|\chi_3|$, appears to be dominated by the field induced reduction of entropy. The spectra of $|\chi_3|$ display maxima at frequencies below those of the loss peak, and the $|\chi_3|$ amplitude increases with decreasing temperature [4]. This behavior can be rationalized by a relatively simple phenomenological model.

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Dielectric spectroscopy and neutron scattering study of colloidal magnetic fluids in electric fields

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Magnetic fluids are suspensions of nanosized magnetic particles (1-100 nm) in appropriate carrier liquids [1]. Those based on transformer oils are in increasing scientific interest due to their enhanced cooling and insulating properties as compared to pure oils. Recently we conducted investigation into magnetic particle aggregation induced by external electric fields [2,3]. The investigated sample was composed of transformer oil Mogul, magnetite nanoparticles, and oleic acid acting as a stabilizing agent. In this paper we report on the use of dielectric spectroscopy and liquid crystal cells as an effective method to reveal the aggregation processes in magnetic fluids under electric fields. Focusing on a low frequency relaxation process, which is supposed to reflect residual ions polarization, we follow the formation of particle aggregates at various sample and electric field conditions. To prove the structural changes of the magnetic fluid in electric field we applied *in situ* small angle neutron scattering method with specially arranged sample environment. It was found that the magnetic nanoparticles reversibly assemble in direct current electric fields higher than a critical field intensity, forming so anisotropic structures greater than 300 nm. The potential role of these aggregates is analyzed in regard to the peculiar high dielectric breakdown field strength of magnetic fluids. Finally, we discuss differences and complementarities of these two techniques in the study of colloidal magnetic fluids in electric fields.

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Field-sensitive electrical properties of oxide ceramics: dielectric breakdown and resistive switching, a common mechanism?

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The bulk electrical properties of a range of electrical ceramics, including acceptor-doped titanate [1] and ferrite perovskites [2], yttria-stabilised zirconia, YSZ [3] and lightly-reduced rutile [4] are sensitive to application of a small bias voltage. The acceptor-doped titanates [1] show a reversible increase in electronic conductivity by one to three orders of magnitude with fields of 10-100 V/cm and at temperatures above about 300 ^{o}C: such materials form the basis of multilayer ceramic capacitors and their enhanced conductivity may be a precursor to dielectric breakdown. Ca-doped bismuth ferrite [2] shows a reversible, insulator-semiconductor transition at room temperature under similar conditions. YSZ shows the reversible onset of electronic conductivity [3[in a material that, under normal circumstances, is an oxide ion conductor and electronic insulator; this may therefore represent the onset of dielectric breakdown in the use of YSZ as a ceramic electrolyte. By contrast, lightly reduced n-type rutile ceramics show an increase in electronic resistance with a *dc* bias [4]. These various results will be summarised and the possibility of a common mechanism for dielectric breakdown and resistive switching discussed.

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Dielectric Relaxation of Supercooled Van der Waals Liquids – Universal Pattern of Behavior

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There are two characteristic features of relaxation behavior of liquids when cooled toward the glass transition temperature, T_g [1]. The first of these is the super-Arrhenius dependence of the structural relaxation times. The objective of this presentation is to show that the structural relaxation times of van der Waals liquids, exhibit a universal pattern of behavior when they are analyzed in terms of fragility concept in the full thermodynamic space. Consequently general rules defining the behavior of isobaric, isothermal and isochoric fragilities are formulated for this class of liquids [2]. Our findings are consistent with the density scaling concept. Moreover, it is experimentally proved that both isothermal and isobaric fragilities are new isomorphic quantities in the power low density scaling regime. Concerning the second property of the relaxation dynamics of supercooled liquids, which is the non-Debye character of the dielectric relaxation function of the α relaxation, we will demonstrate that the width of the α-loss peak at or near T_g is strongly anticorrelated with the polarity of the molecule [3]. The larger the dielectric relaxation strength $\Delta\epsilon(T_g)$ of the system, the narrower is the α-loss peak. The correlation is supposedly universal because data from practically all studies by dielectric relaxation in the past decades are included into the consideration. This remarkable property is explained by the contribution from the dipole-dipole interaction potential to the attractive part of the intermolecular potential, making the resultant intermolecular potential more harmonic, and the frequency dispersion of the α relaxation narrower.

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Extracting new information from dielectric spectroscopy by keeping track of geometric changes of the capacitor

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"Glass and Time", IMFUFA, DSE, Roskilde University

In studies with dielectric spectroscopy the focus is often on the time scale and shape of the relaxation while less attention is given to the absolute value of the measured capacitance and the derived dielectric constant. In fact, the absolute value is often not given with very high precision because the spacing between the electrodes and the degree of filling will vary as temperature, pressure or other external parameters are changed. In this talk we present two examples, where the geometry of the measuring capacitor is controlled and modelled in detail in order to extract new types of information from dielectric spectroscopy.

The first example is a method for measuring the dynamical expansion coefficient of glass forming liquids. In this technique the sample is placed in a parallel plate capacitor such that the sample maintains the spacing between the plates. Thus a change in sample volume in response to a temperature change leads to a change of the capacitance. The advantage of this technique is that capacitances can be measured with very high precision, and the small density changes associated with linear experiments can therefore be determined reliably. The method is based on earlier work by Bauer *et al* [Phys. Rev. E 61, 1755 (2000).] on polymers, but modified to work with molecular liquids and extended in the dynamical range as well as the precision.

In the second example we study the amplitude of the dielectric signal at elevated pressure using a steel capacitor with saphire spacers, which makes it possible to keep the geometric capacitance constant within less than 0.3% while changing temperature in the range 260-320 K and going up to 300 MPa in pressure. This allows us to test and confirm predictions from the isomorph theory regarding the invariance of molecular orientational correlation along isochrones in the pressure-temperature phase diagram. Measurements are performed on the van der Waals bonded liquid 5PPE, which has also been shown to comply to other isomorph predictions.

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Qualitative change in structural dynamics of some glass-forming systems

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Analysis of temperature dependence of structural relaxation time τ_α (T) in salol and some supercooled liquids revealed a qualitatively distinct feature - a sharp, cusp-like maximum in the second derivative of log $\tau_\alpha(T)$ at some T_{max} [1]. It suggests that the super-Arrhenius temperature dependence of $\tau_\alpha(T)$ in glass-forming liquids eventually crosses over at decreasing temperature to an Arrhenius behavior at $T<T_{max}$, and there is no divergence of $\tau_\alpha(T)$ at non-zero T. In some other glass-formers, e.g., based on hydrogen bonding, T_{max} is predicted to be below glass transition temperature T_g and thus it is unobservable. The position of T_{max} with respect to T_g depends on sensitivity of τ_α to change in liquid's density quantified by the exponent γ in the scaling $\tau_\alpha \sim \exp(A/T\rho^{-\gamma})$. We show that $T_{max} > T_g$ if $\gamma > 3.5\div4$. According to the elastic model of the glass transition [2], log $\tau_\alpha(T)$ is proportional to the infinite-frequency elastic moduli. We found that the bulk and shear moduli of salol at GHz frequencies have the peculiarities of the second derivative on temperature at T_{max} that confirms the tight relation between the elastic moduli and log τ_α. These results might turn the discussion of the glass transition to the new avenue – the origin of the limiting activation energy for structural relaxation at low T.

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Entropic models and their prospects for an universal description of dielectric phenomena near the glass transition

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Starting from the commonly known Adam-Gibbs model, which has become one of the most discussed models of the thermodynamic evolution of the characteristic time scale of molecular dynamics of supercooled liquids near the glass transition, entropic grounds for the molecular dynamics reflected in the structural relaxation have been highly appreciated. Nevertheless, such entropy based models have not enabled yet to make a final breakthrough in the universal theory of the glass transition and related phenomena that occur near this transition from the metastable supercooled liquid state to the non-equilibrium glassy state. In recent years, we have made a progress in developing a few entropic models based on both the configurational entropy S_c [1,2] and the total system entropy S [3] as functions of temperature T and volume V. By using the broadband dielectric spectroscopy (BDS), which is an excellent method for exploring over a dozen decades of the time scales of molecular motions, we have thoroughly verified the T-V entropic models in the wide range of the molecular dynamics time scale, which has been defined by the structural relaxation time τ and determined from BDS measurements in ambient and high pressure conditions. As a consequence, we have established and experimentally tested important relationships between the time scale τ of molecular dynamics and the configutational and total entropies, S_c and S, which bear some universality hallmarks. Besides these undoubdeted achievements, we also intend to present the latest results of our recent studies, which show some material-dependent limitations of the entropic models based on S_c and S as well as prospects of applying the models to fitting the contribution from the sctuctural relaxation process to dielectric loss spectra.

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Segmental mobility at the glass transition in poly(ethylene-vinyl acetate) copolymers : Comparison of two approaches.

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This work reports new experimental results focused on Modulated Temperature Differential Scanning Calorimetry (MT-DSC) and Broadband Dielectric Spectroscopy (BDS) investigations. Two different models, based respectively on the four point dynamic susceptibilities [1] and the thermodynamic fluctuation approach [2], have been used to compare the evolution of the cooperativity length during the α-relaxation process. The first model allows to estimate *Nc* the number of dynamically correlated molecules during the α-process, and the second one allows to estimate N_α the number of structural units in a Cooperative Rearranging Region (CRR). But, does it exist a clear difference between *Nc* and N_α?

In a previous work concerning different fully amorphous polymers with different backbones, we observed a huge impact of the molar mass of the relaxing units by comparing *Nc* and N_α [3]. But the chemical structure of the studied systems was very different and we only put in evidence two tendencies related to low and high molar masses.

In this new work, our motivation is to examine *Nc* and N_α with time and temperature variations in amorphous copolymers of poly(ethylene-*co*-vinyl acetate) (EVA) with different vinyl acetate content (VAc): from PVAc (100 wt.% VAc) to EVA50 (50 wt.% VAc). This sample family presents the advantages to have the same backbone but different number of dipolar pending groups, i.e. different inter-chain dipolar interactions having a clear influence on the CRR size, but no influence on the fragility index value as shown recently [4].

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Ultra-confinement: The Mysteries of Ancient Water Imprisoned in sub-nano channels in Natural Minerals

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The water molecule is a conundrum of physics. A seemingly simple molecule with a not very impressive dipole moment, it is a delinquent in every sense of the word. Exhibiting over 64 anomalous behavioral traits, much of this behavior can be linked to its ability to form Hydrogen bonds and complex liquid structures. Yet it can be tamed of sorts by imprisonment. Certain naturally occurring minerals, such as Beryl and Cordereite, contain sub-nano diameter channels as an integral part of the crystal lattice. The diameter of these spaces is often of the same order of magnitude as the diameter of a water molecule, 4-5 Å. Under such conditions water entrapped in them at the time of formation (hence “Ancient”), but not chemically bound, can no longer behave as “water”. But rather than conform, these extreme conditions lead to unusual behaviours. Concepts like H-bonding and clustering are now not relevant and a new class of dynamics must arise for these molecules. These crystals are, per force, highly anisotropic, leading to very different dielectric properties depending of the crystal axis chosen. DC conductivity is sometimes present, but not necessarily along the water channels. In this paper we shall explore some of these consequences.

Water confined in nanoporous alumina: Ice nucleation, Kinetics and Dynamics

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Liquid water can be supercooled down to -38 ^{o}C, known as the limit of homogeneous nucleation. In most cases, however, water will freeze at higher temperatures by impurities via heterogeneous nucleation. However, despite fundamental importance in science and technology control of heterogeneous, and more importantly, of homogeneous nucleation at atmospheric conditions remains a challenge. Here we show that the nucleation mechanism of ice can be precisely regulated by confining water within self-ordered nanoporous aluminum oxide (AAO). With DS we found a transition from heterogeneous nucleation of hexagonal ice to homogeneous nucleation of predominantly cubic ice (I_c) with decreasing pore diameter. These results lead to a phase diagram of water under confinement.[1] Subsequently, we invstigated the kinetics of ice nucleation in confinement using DS as a probe. Both heterogeneous and homogeneous nucleation, obtained at low and high undercooling respectively, are stochastic in nature. The temperature interval of metastability extends over ~ 4 °C and 0.4 °C for heterogeneous and homogenous nucleation, respectively.[2] DS further revealed two dynamic processes under confinement. With respect to the dynamics, two processes (“fast” and “slow”) with an Arrhenius temperature dependence are attributed to ice and supercooled water relaxation, respectively. The main relaxation process of ice under confinement (“slow” process) has an activation energy of 44±2 kJ/mol.[3] The latter is in agreement with the reported relaxation times and activation energy of cubic ice prepared following a completely different route (by pressure).[4]

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The interplay between water and solute

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Whenever the water molecules interact with either dipolar or charged systems, the main water dielectric relaxation peak broadens, resulting in a Cole-Cole (CC) relaxation, $\varepsilon^*(i\omega) = \Delta\varepsilon/(1+(i\omega\tau)^{\alpha})$, where $\Delta\varepsilon$ is the dielectric strength, τ is the characteristic relaxation time and $0 < \alpha < 1$ is the broadening parameter. If a solute is dipolar in nature, new solute-water clusters are created due to dipole-dipole interactions. It leads to the “red shift” of the dielectric loss maximum frequency. In the case of ionic solutions, another cluster structure develops, due to dipole-charge interactions and a “blue shift “is observed. In the general case when a solute molecule has both charged and dipole groups, the dielectric loss maximum demonstrates a “red” or “blue” shift, depending on the entity concentration. In all aqueous solutions, the water-solute interactions can be considered as dipole-matrix interactions in which water is the dipole subsystem. The phenomenological 3D trajectories approach [1] was applied to the results of isothermal dielectric measurements of different concentrations of the following aqueous solutions:

- Hydrocarbons (Glucose and Fructose) [2]
- NaCl and KCl, the most physiologically significant salts [3]
- AMP and ATP, the important energy molecules [4]
- Amino Acids [5]
- Myoglobin [6]

The CC parameters of the main water peak define a trajectory that can clarify the nature and rate at which water interacts with the solute. Additionally, changes in the trajectory indicate the solute concentration regions where dipole-dipole or dipole-charge interactions dominate. In this paper, we extend this approach from comparatively simple protein solutions to the complexity of Red Blood Cells (RBC) suspensions by monitoring the RBC cytoplasm under different external conditions. Dielectric measurements of RBC suspensions in the frequency region of 100 MHz to 50 GHz as a function of aging or external glucose contartion also reveal a distinct time point or glucose concentration after which the spectra are radically changed.

The conclusion is that the dielectric response of the cytoplasm in microwaves is due to the water therein and its interaction with physiological actve components in cytoplsm. This opens a window of opportunity to exploit this for the non-invasive monitoring of diabetes or to non-invasive control of the quality of Stored RBC in a Blood bank in order to manage the inventory.

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Dielectric Study of Aqueous Solutions of Collagen Extracted from Tilapia Scale

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Collagens are the major proteins of the extracellular matrix supporting biological structures such as bone and skin. Since process of self-assembly of collagen molecules into fibril is considered to be very useful in the regenerative medicine, the application studies are extensively performed especially in the medical area. Recently, attention is focused on collagen molecules extracted from fish because of avoiding risks of zoonosis.

Usual collagens from fish are not soluble in water and this property is not very useful in applications. However, collagen extracted from fish scale of tilapia (Oreochromis Niloticas), tilapia collagen (1.5nmϕ x 300nm, M_w=300k), is water-soluble, therefore, many researches for the practical applications are being proceeded. One of the points is large viscosity of aqueous solutions of tilapia collagen. It has been speculated that this property comes from existence of large amount of bound water suggested in dielectric studies for aqueous solutions of globule proteins [1-2]. However, no one has provided scientific evidence to explain such story.

We have investigated dielectric properties of aqueous solutions of tilapia collagen by means of time domain reflectometry (TDR) in the frequency range of 200M-20GHz to evaluate the solution dynamics. It has been found that there is no expected difference between dielectric dispersions of 0.4wt% tilapia collagen aqueous solution and pure water, even the value of viscosity of the solution is 70 [mPa s] which is 70 times larger than that of water. We also studied the solution with amino acids to evaluate microscopic viscosity. It is well known that aqueous solution of amino acids shows dielectric relaxation process around 100M-1GHz and the value of relaxation time can be well described by the Stokes-Einstein-Debye law employing the viscosity of bulk water [3]. It has been found that relaxation frequencies of the process of amino acids for both the tilapia solution and the pure water are the same as each other. These experimental results indicate that interaction between water and collagen molecules is not very strong and the most of water in the solution is free water. The high viscosity of the solution is due to a kind of network structure composed of collagen molecules and such netwoek folds usual water.

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Dynamical and Structural Study of n-Lysine´s Oligomers

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Proteins are dynamic systems which constantly fluctuate to perform a biological function. Depending on the enviroment, proteins are surrounded by a hydration shell, one or two layers of water, with properties different from bulk water. Without water these *machines* are not working properly and no functionality is possible.

The literature regading proteins and water is extensive but the dynamical aspects are still not well understood. In particular, the solvent-protein coupling is still controversial: some researchers claim that the most important protein motions seem to follow the same temperature dependence as the water motions (*slaving*). Another view is that water plasticizes the protein or even that there is a mutual effect on both water and protein dynamics.

In this work we present a dielectric study of aqueous solutions of n-lysine´s oligomers (n = 1 to 10) and ε-Poly-L-lysine analysed to a concentration of c_w = 40 wt% (in weight). Structurals characteristics of these samples were analyzed by FTIR and SAXS. With regards to the dynamics, our experimental evidence supports that the conformational dynamics of the oligomers is determined by the water dynamics, in a similar way as previously observed for solvated proteins. The results show that this behavior is independent on any structural differences in the peptide chains (i.e. chain-length, the secondary structure adopted or the number of carbon atoms in the main chain) and on the peptidic glass transition. These findings indicate that water may have a universal role for macromolecular dynamics.

Dynamics of water, solute, and ice in partially crystallized aqueous solutions studied by broadband dielectric spectroscopy

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The glass transition phenomena in aqueous solutions without crystallization of water have been investigated extensively and universal propreties of water at temperatures down to the glass transition temperature, T_g, of water have been invoked. However, partially crystallised aqueous solution have been studied rarely, since the crystallization of water make the solutions complex. In addition, the thermal history effect strongly to experimental results.

Dielectric relaxation processes originated from uncrystallized water (UCW)(process I), ice (process II), and hydrated solute (process III) were investigated by broadband dielectric spectroscopy at subzero-temperatures down to 113 K for partially crystallized aqueous solutions of hydrophilic synthesized polymers, proteins, and sugars.

UCW is the water which is in the liquid state even at subzero tempertures, and it can be observed as process I at the highest frequency in the three relaxation processes. The relaxation time, τ, and strength, $\Delta\varepsilon$, of the relaxation of UCW is reflected the interaction between water and solute molecules. The differences of τ and $\Delta\varepsilon$ of UCW on solute molecular structure are emphasized if compared to those of watert above the melting temperature of ice. The solute concentration in liquid phase can be obtained from $\Delta\varepsilon$ of UCW and it visualises the freeze-concentration process under melting/crystallization on temperature-composition diagram together with T_g obtained from τ of the α-relaxation.

τ of ice is affected not only by the macroscopic thermal history but also by the hiostory of microscopic grouth speed of ice. For pure water, slow crystallization of ice makes larger relaxation time, and the faster crystallization make the relaxation time of ice smaller. τ of ice depends on the strucuture of solute molecule and solute concentration in aqueous solutions. Sometimes, multiple relaxation processes of ice appear and it seems to reflect the heterogeneity in crystallized ice in solution.

The process III observed at the lowest frequency in these three relaxation process is considered to be origimated from molecular motion of hydrated solute. T_g measured by thermal analysis agree well with the temparature, at which the relaxation time of process III is 100 s – 1000 s. It implies that the process III is related to the structual relaxation, i.e., the α-relaxation. On the other hand, Arrhenius to non-Arrhenius transition of the temperature dependence of τ of UCW occures at the T_g. This relationship between the relaxation processes of UCW and hydrated solute are common to that observed in non-crystallized aqueous systems and other glass formers.

Water dynamics in Hyaluronic Acid hydrogels

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Hyaluronic acid (HA) is a high molecular weight biopolysacharide occurring naturally in all living organisms. HA is used in several biomedical applications due to its high hydrophilicity, biocompatibility and biodegradability. Due to the significance of this molecule for biological procedures a variety of commercially available preparations of HA derivatives and cross-linked HA materials have been developed for drug delivery and an extraordinary broad range of biological applications. For such biomedical applications the study of the dynamics of water interacting with HA cross-linked materials is of great significance [1].

Water dynamics in hydrated hyaluronic acid (HA) hydrogels crosslinked by divinyl sulfone (DVS) were studied by differential scanning calorimetry (DSC), dielectric relaxation spectroscopy (DS) and thermally stimulated depolarization currents (TSDC) techniques. The samples covered a wide range of composition, from to practically dry membranes to swollen solid samples (65wt% of water). Crystallization and melting of water were studied by DSC and the amount of uncrystallized water was calculated. The evolution of dynamics with hydration level was followed for several dielectric relaxations, the emphasis being given to relaxation processes related to hydrogen bond network of water molecules with and without the presence of crystalline ice phase.

Our results shed light on the interplay between the mobility of the polymer polar groups and the relaxation of uncrystallized water molecules themselves. A relationship between the protonic conduction mechanism and the relaxation processes of polar groups and uncrystallized water molecules (the so-called water ν process or universal β-relaxation of water) has been found. Contributions originating from water molecules in excess (uncrystallized water clusters or ice), follow separate relaxation modes slower than the ν relaxation. Our study focus on the determination of the specific features of liquid-like water clusters as compared to those of the ice-like networks of water molecules.

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Molecular dynamics in nanometric confinement

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The impact of external and internal geometrical constraints [1,2] on the molecular dynamics of polymers are studied for a variety of different experimental conditions, (i) polymer brushes in the dried [3] and swollen [4] state and polymers [5,6] and low molecular weight organic glasses [7] in (ii) nanometric thin layers and (iii) in nanopores.

(i) The molecular dynamics of poly(2-vinyl-pyridine) (P2VP) brushes is measured by Broadband Dielectric Spectroscopy (BDS) in a wide temperature (250 K to 440 K) and broad spectral (0.1 Hz to 1 MHz) range. This is realized using nanostructured, highly conductive silicon electrodes separated by silica spacers as small as 35 nm. A "grafting-to"-method is applied to prepare the P2VP-brushes with five different grafting densities (0.030 nm2 to 0.117 nm2), covering the "true-brush" regime with highly stretched coils and the "mushroom-to-brush" transition regime. The film thickness ranges between 1.8 to 7.1 (+/- 0.2) nm. Two relaxations are observed, an Arrhenius-like process attributed to fluctuations in the poly(glycidyl-methacrylate) (PGMA) linker used for the grafting reaction and the segmental dynamics (dynamic glass transition) of the P2VP brushes. The latter is characterized by a Vogel-Fulcher-Tammann dependence similar to bulk P2VP.

(ii,iii) Broadband dielectric (BDS) and Fourier transform Infrared (FTIR) spectroscopy are employed to study molecular dynamics of polymethylphenylsiloxane (PMPS) in 1-D and 2-D geometrical constraints. PMPS under the former confinement of thin films down to thickness of 7 nm spin cast on highly conductive silicon wafers in combination with nanostructured counter electrodes are studied by BDS while in the latter case, PMPS infiltrated into porous silica membranes with unidirectional nanopores having diameters down to 4 nm are probed by both BDS and FTIR. The glass transition temperature (Tg) of thin films for all the thicknesses investigated remained bulk-like but the Tg decreases with the reduction of pores sizes for 2-D confinement where an additional interfacial relaxation process is observed. This change in Tg is attributed to a reduction in density of bulk-like molecules at the center of the pores. The intra-molecular IR vibrations of different moieties show dissimilar T-dependencies and are influenced by both confinement and surface effects. Intermolecular dynamics of PMPS is therefore impacted by the dimensionality of the confinement.

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Non-equilibrium kinetics of the segmental dynamics of 1D confined polymer melts

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The current view on the deviation from bulk behavior of soft matter confined at the nanoscale level focuses on the balance of finite size effects and interfacial interactions in systems at thermodynamic equilibrium. For example, thin polymer films (thickness typically below 100 nm) are treated as slabs where the bulk molecular dynamics is locally perturbed by the presence of free surfaces (~ 2 nm layer at the interface with air, other gases or vacuum) and adsorbing interfaces (proximity of non-repulsive wall). A reduction in the glass transition temperature, T_g, is commonly imputed to the faster dynamics of free surfaces, while the presence of an adsorbing interface is considered as a source of slower molecular modes.

Such a picture, although very intuitive, cannot describe the peculiar features of soft matter under confinement, including exotic phenomena like the increase in Tg at the free surface of star-shaped polymers and the reduction in Tg of capped films (no free surfaces), in several nanocomposites and in adsorbed layers. It is obvious that one or more key parameters are still missing in our understanding of confined systems.

Based on our previous experimental evidence [1], we demonstrated that the glass transition temperature of freshly spincoated films, equilibrated at the timescale of reptation, evolves during annealing in the liquid state, following the kinetics of adsorption until recovering bulk value (equilibration).

In this talk, we present novel experimental evidence – from ellipsometry, fluorescence spectroscopy and broadband dielectric spectroscopy – supporting our hypothesis on a mechanism of equilibration mediated by irreversible adsorption. In particular, we show that annealing at the timescale of adsorption cancels tremendous reductions in T_g as large as 40 K in films with one free surface, and reduce by almost one order of magnitude the enhancement in segmental mobility in capped layers. Furthermore, we verified that the mechanism of equilibration of thin polymer films do not strictly follow the free volume content/molecular mobility/aging rate cycle commonly observed for non-equilibrium bulk melt. On the contrary, the adsorption kinetics, and not segmental mobility, is the driving force of the time evolution of the confinement effects. A new molecular mechanism is proposed.

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Electrode Polarization and Glassy Dynamcis in Thin Films of Polyamide Random Copolymers

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Glass transitions in thin films have been widely investigated to determine the confinement effect on the glass transition dynamics. The dependence of the glass transition on the film thickness has been investigated mainly for nonpolar polymers. In contrast, the glass transition dynamics of thin films of strong polar polymeric systems have not yet been investigated intensively. Polyamides are one of these strong polar polymers. In this system, two dielectric signals are observed at high temperatures, the alpha-process and the relaxation process due to electrode polarization (EP-process). We investigate the relaxation behavior of thin films of polyamide random copolymers by dielectric relaxation spectroscopy to elucidate the confinement effect on glassy dynamics in strong polar polymeric systems [1].

The temperature dependence of the relaxation rate of the EP-process and the alpha-process has been measured for thin films of PA66/6I with various film thicknesses, and is found to have a Vogel-Fulcher-Tammann (VFT) type of temperature dependence. This suggests that the molecular motion due to the EP-process should be associated with the alpha-process, i.e., segmental motion of the polymeric system. The glass transition temperature *Tg* was evaluated from the EP process. The *Tg* obtained thus exhibits a slight decrease with decreasing film thickness. Furthermore, the fragility index *m* was derived from the temperature dependence of the relaxation time of the EP process, and the value of *m* increases with decreasing film thickness.

The EP-process is originated from the motion of the charge carriers in polymeric systems. Hence, the diffusion constant and concentration of charge carriers could be evaluated from the relaxation time and the dielectric strength on the basis of a molecular model of the EP-process [2]. The diffusion constant *D* of charge carriers can be described by a VFT equation and *D* does not have any thickness dependence down to ca. 100 nm, while *D* increases with decreasing film thickness below 100 nm. This suggests that there is an intrinsic acceleration of diffusion motion, i.e., the translational motion of charge carriers in thin films.

We made dielectric measurements on thin films of polyamide random copolymer PA66/6I and PA106/10I. The EP-process could be observed in addition to the alpha-process, and the glass transition temperature could be evaluated from the temperature dependence of the relaxation rate of the EP-process. The *Tg* exhibits a slight decrease with decreasing films thickness. The diffusion constant of the charge carrier and its intrinsic thickness dependence could also be evaluated from the EP-process.

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Effect of Confinement on Segmental Relaxations in PBAC/PETg Multi-layered Films

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In a recent decade, the segmental relaxations in multi-layered films have been broadly studied[1–3]. Reducing the size of a glass former from micro to nanoscale is possibly accompanied by a significant deviation of the structural and dynamical properties with respect to the bulk. In this work, the influence of thickness reduction on the glass transition temperature (T_g) and the segmental dynamics in multi-layered films of PBAC/PETg have been investigated.

The combination of BDS and MT-DSC measurements enables the calculation of the average values of cooperatively rearranging region (CRR)[4,5] on the whole temperature range of segmental relaxations.

Moreover, the influence of the layer thickness reduction on the glass transition temperature, the super-Arrhenius behaviour of the segmental relaxations, and the dynamic fluctuations in the supercooled liquid will be discussed for the two amorphous polymers.

Confinement effects have been identified for layer thickness lower than 100 nm and result in very different and non symmetrical variations of the relaxation parameters for PBAC and PETg.

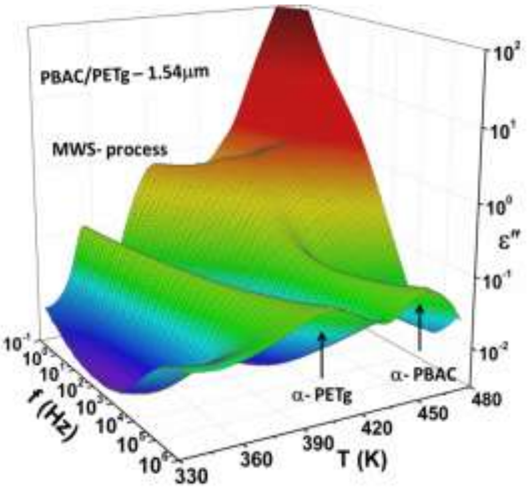

Figure 1 : 3D plot of dielectric loss vs frequency and temperature for PBAC/PETg multi-layered film: layer thickness 1.54 µm

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Dielectric and Thermal Relaxation Behavior of Ultra-Thin Films of Poly(vinyl methyl ether) – Evidence of an Adsorbed Layer

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Despite the many controversial discussions about the nanometric confinement effect on the properties of ultra-thin films, much remain not understood and/or experimentally unproven. Here, a combination of Broadband Dielectric Spectroscopy (BDS) and Specific Heat Spectroscopy (SHS) employing AC nanochip calorimetry were utilized to investigate the glassy dynamics of ultra-thin films of a low M_W Poly (vinyl methyl ether) (PVME) (thicknesses: 7 nm – 160 nm). For BDS measurements, a recently developed nano-structured electrode sample arrangement is employed; where ultra-thin films are spin-coated on an ultra-flat highly conductive silicon wafer, sandwiched between a wafer with nanostructured SiO2 nano-spacers with heights between 35 nm and 70 nm. For films with thicknesses up to 50 nm, BDS measurements showed two relaxation processes, which can be analyzed for these film thicknesses in details. The process located at higher frequencies coincidence in both, its position and temperature dependence, with the α-relaxation of bulk PVME and is therefore assigned to the α-relaxation of a bulk-like layer. The temperature dependence of the relaxation rate of this process in independent of film thickness. This is further confirmed by the SHS investigations, which superimpose in its temperature dependence with the BDS results; independent of film thickness. The second process is located at lower frequencies, where it shows a different temperature dependence and ascribed to the relaxation of polymer segments adsorbed at the substrate. The interaction of PVME with SiO_2 was further confirmed by contact angle investigations. This adsorbed layer further undergoes a confinement effect that results in a lower Vogel temperature than that of the bulk-like layer. A detailed analysis of the dielectric strengths of both processes reveals that the thickness of the adsorbed layer decreases with increasing temperature, while that of the bulk-like layer increases. As a main conclusion, BDS showed that the glassy dynamics of the bulk-like and the adsorbed layer are thickness independent, which is in agreement with the SHS results. To our knowledge, this is the first probing of the segmental dynamics of an adsorbed layer in ultrathin films.

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Some Overlooked Effects in Dielectric Phenomenon

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Dielectric spectroscopy has helped us make significant advances in elucidating the relaxation dynamics. However, its use for studying the effect of the equilibrium permittivity, ε_s, on dipolar fluctuations and ionic diffusion dynamics has been overlooked. I will attempt to describe three of these oversights, as follows:

1. The change in ε_s with change in the temperature T and the pressure p affects the ionic-equilibrium, as well as affects the ion-pair separation. This in turn changes the dc conductivity, causing it to deviate from its thermally-activated behavior expected from change in the ionic mobility with change in T and p.
2. Variation of ε_s with T is related to the variation of the entropy of a dipolar liquid under a fixed electric field, E. The E-induced decrease in the entropy is taken to indicate ordering from polarization of dipolar molecules, different from the change in the density and short-range structural fluctuations in dipolar liquids. The nature of the ordering can be investigated by a combination of experiments performed for measuring the high-E and high-p effects on the dielectric relaxation time, and it can be shown that the E-induced ordering is consistent with the type of ordering that occurs on cooling or pressurizing a liquid, and that a high E would decrease the strength of the JG relaxation. Thus thermodynamics of an electret is related to $(d\varepsilon_s/dT)_p$; its entropy varies as E^2 ; and there is a pressure equivalnce of the E-induced entropy decrease.
3. Electrical measurements do not distinguish between the polarization and conduction currents. Therefore, models are used to separate the two currents by analyzing a given set of data usually in the M^* and Z^* quantities. They can also be analysed after conversion to ε^*, and Y^*. Self consistent analysis of the data in the M^*, Y^*, and Z^* should yield the same distribution parameter for the conduction process if ε^* contributions from dipolar molecules and ion-pairs can be accounted for. Doing so requires determining ε_s from a feature-less permittivity spectra. Fast measurements and data analysis now allow one to resolve the geometry-dependent Warburg impedance that overwhelms the ε^* features , and thereby to obtain the ε^* dispersion and absorption when none is seen in the measured data.

Atomic origin of barriers for ionic transport through interfaces

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The performance of Solid Oxide Fuel Cells is known to be strongly limited by the presence of interfaces or grain boundaries. Space-charge regions generated by mobile ions are believed to be responsible, due to the resulting electrostatic barrier for ion transport. We show that something different is at play by studying ion transport in a bicrystal of yttria (9% mol) stabilized zirconia (YSZ). Contrary to expectations from the conventional space-charge model, we find no evidence of a long-range O vacancy depletion layer. Scanning transmission electron microscopy (STEM) provides evidence of Y segregation to the grain boundary at Zr sites, together with a depletion of oxygen that is confined to a small length scale of around 0.5 nm. Combining broadband dielectric spectroscopy (BDS) measurements, nanoscale electrochemical strain microscopy (ESM), and density functional calculations, we are able to study ion transport across a single grain boundary. We conclude that besides the possible effect of the modified chemical bonding at the grain boundary, a negative charge resulting from grain-boundary-induced acceptor states gives rise to an additional barrier for ion transport.

Intra and inter-molecular dynamics in poly(ethylene glycol) derivatives under confinement

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Broadband dielectric and Fourier-Transform Infrared spectroscopy are combined to study the molecular dynamics of two glass forming systems:poly(ethylene glycol) phenyl ether acrylate (PEGPEA), and poly(ethylene glycol) dibenzoate (PEGD), confined in unidirectional, non-interseting nanopores of mean diameters 4, 6 and 8 nm. The *intra*moleucular mobility is revealed by analysing the temperature dependencies of positions and intensities of specific IR absorption bands and compared with *inter*molecular dynamics obtained by means of dielectric measurements. We show that pore sizes affect the motion of different moieties (e.g phenyl rings, acrylates) which also influence the segmental dynamics of ethylene glycol. The information obtained in this way gives new insight to description of the glass transition in restricted geometry.

Peculiar behavior of the dynamics of confined liquids. The role of negative pressure

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Broadband Dielectric Spectroscopy (BDS) was applied to study dynamics of four different simple liquids at various thermodynamic conditions and under spatial 2 D confinement. As a complementary also Positron annihilation lifetime (PALS) measurements weere carried out for bulk 2-ethylhanol and sample confined in native silica nanopores. All these meeasurements indicated unquestionably that significant enhancement of the dynamics of the confined molecules at low temperatures is related to the vitrification of the interfacial molecules (T_{gint}) affecting the packing density of the core molecules. This is corroborated by the PALS measurements which demonstrated that the effective volume for the confined samples is slightly higher and seems to be temperature invariant below T_{gint}. As a consequence of that negative pressure systematically develops reaching value p= -80 MPa and -110 MPa (dependently on the pore size and the kind of porous material) at the glass transition temperature. Interestingly it was also found that the sensitivity of various glass-forming liquids to the “confinement effects” can be rationalized by considering the relative importance of thermal energy and density contributions in controlling the α-relaxation dynamics (the Ev/Ep ratio). This result offers a better understanding of counterbalance between surface and finite effects as well as the role of negative pressure in controlling dynamics and the glass transition process for liquids under 2D spatial restrictions.

Studies on the Temperature and Time Induced Variation in the Molecular Dynamics of Low and High Molecular Weight Glass-Formers at the Nanoscale.

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The effect of 2D confinement on the molecular dynamics of triphenyl phosphite (TPP) and poly(propylene glycol) (PPG) has been studied with the use of Broadband Dielectric Spectroscopy (BDS) and Differential Scanning Calorimetry (DSC). It is shown that all observed realaxation processes become faster with increasing degree of confinement. Interestingly, it is found that the crossover from VFT to the Arrhenius-like behavior of molecular dynamics is strictly related to vitrification of the adsorbed polymers and freezing of the system's density. We report also that the mean relaxation times of the normal, τ_{NM}, and segmental modes, τ_α, depend on thermal history of confined PPG and can be significantly modified using different thermal treatments. In addition, we demonstrate that annealing of the samples below the crossover temperature, T_c, leads to a systematic shift of the examined modes towards lower frequencies, resulting in an increase in the glass transition temperature of the spatially restricted materials. Taking into account recent studies, we believe that this new experimental observation is most likely related to the equilibration of systems' density: after annealing, a system with higher density characterized by more homogeneous dynamics can be obtained. It is therefore possible to modify and control properties of the confined material by using different thermal treatment protocols. Our results offer a better understanding of the behavior of the spatially restricted soft matter and the interplay between mobilities at two completely different length scales.

Devices and Material characterization from DC to mm-wave and THz

Giovanni D'Amore, Say Phommakesone

Keysight Technologies

From stealth materials to dielectric substrates, microwave food products to biofuels, accurate characterization of their electromagnetic properties at microwave and mm-wave frequencies provide engineers with critical information needed for material and circuit design, modelling, research, manufacturing and quality control. In this paper, we will overview the classes of methods employed to measure the dielectric properties of solids and liquids and will discuss the criteria one should consider when selecting a measurement technique. The focus will be on those techniques useful for measuring the relative permittivity and loss tangent of dielectric materials, both liquid and solid, over a frequency range that covers 100 MHz to 1.1 THz.

Broadband Dielectric Spectroscopy – Technical Aspects of Today and Tomorrow

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Broadband dielectric spectrometers require top-class frequency response analyzers with ultra-wide impedance range, extreme tan δ accuracy and resolution, easy-to-use sample cells with good isolation properties and low background, a reliable temperature control system and a versatile software package for experimental setup and data analysis.

On the user side, proper sample preparation (including suitable dimensions) and contacting as well as some technical background and understanding of data interpretation increase the chance of obtaining high-quality measurement results.

In this contribution, we intend to address two issues:

- The technological direction of BDS – which are the essential features of state-of-the-art broadband dielectric spectrometers of today and tomorrow? Which improvements are needed, and what can be achieved in the near future?
- What can the user do to improve the results? We will discuss pitfalls to avoid as well as recommended procedures based on exemplified cases supplied by our customers.

Extracting Differential Capacitance Values of the Ionic Liquid-Au(111) Interface from Impedance Data using the RelaxIS Impedance Spectrum Analysis Software

Jens Wallauer, Marcel Drüschler

rhd instruments GmbH & Co KG

Interfacial processes between electrodes and ionic liquids (IL) have become a major research topic in the last years. Due to outstanding, tuneable physico-chemical properties, IL are promising candidates for the usage as electrolytes in many applications like batteries, super capacitors or solar cells.

An important physical quantity of interfaces is the differential double layer capacitance, which is a measure of change in stored charge in the interface caused by a change of the electrode potential. This quantity can be compared with theoretical predictions from theories as well as DFT, MD or MC simulations, making it an essential tool in the validation of the models.

The differential double layer capacitance at well defined metal surfaces can be measured using dc biased impedance spectroscopy. In this study, the room temperature IL [Pyrr$_{1,4}$]FAP in contact with a Au(111), single crystalline working electrode was measured. It was found that in the cathodic domain, where the double layer capacitance should be dominated by cationic interactions, multiple capacitive processes on different timescales take place, which may be explained by cation rearrangements or site exchanges between ions [1,2,3].

This talk outlines the experimental setup using a Microcell HC cell stage equipped with a TSC Surface measurement cell developed by rhd instruments [4]. It furthermore gives a detailed explanation of the data analysis procedure using the RelaxIS software (distributed by rhd instruments). The software extracts the differential capacitance of the different processes using a fit of a Havriliak-Negami function to the measured spectra in the complex capacitance plane, which is superior to single frequency measurements in various ways. Finally, further features of this user-friendly, convenient to use and comprehensive software package are shortly outlined.

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[4] For further information regarding design and functionality of measuring cells, see https://www.rhd-instruments.com.

High Voltage Dielectric Spectroscopy on LDPE films

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Dielectric spectroscopy measurements are widely utilised in the electric power industry, since they provide valuable information during the selection or development of new materials, as well as to improve the insulation design, processing, quality, and control of a product. The determination of the dielectric properties is typically done under low voltages, usually only few volts, associated with far lower electric fields (at most a few V/mm) compared to the ones the material will be exposed to during service (kV/mm range).

This contribution discusses high voltage dielectric spectroscopy measurements (HVDS) on low density polyethylene (LDPE) films (≈ 100μm thick), a polymer of particular interest since it serves as the base material for the cross-linked polyethylene (XLPE) employed, e.g., in high voltage cables.

Measurements were conducted in a broad frequency band (10^{-2} to 10^{4} Hz), and in large temperature (-150 to 70°C) and field ranges (10^{4} to 10^{7} V/m), both AC and AC with superimposed DC bias, using a Novocontrol Alpha Analyzer with HVB 4000 interface.

Characteristic examples of such measurements are provided in Figure 1, where the dielectric losses (ε'') as a function of frequency are shown for various AC levels at 70°C. The low frequency region (< 1Hz) is dominated by conductivity contributions. The field dependence of the conductivity "tail" is also apparent. The most interesting finding is on the middle frequency region (10^{0} to 10^{2} Hz), where a jump in ε'' is observed at high fields (threshold between 7 and 8 kV/mm AC fields). The aforementioned results will be discussed in terms of the "flat" loss model proposed by Jonscher [1].

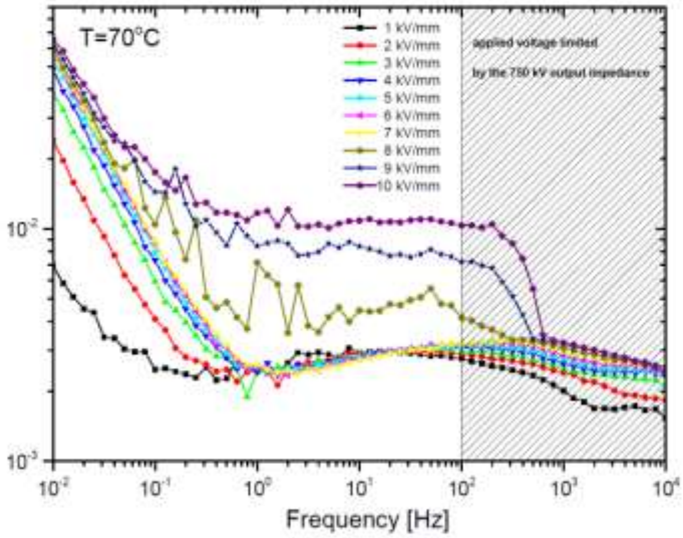

Figure 1 Dielectric losses (ε'') as a function of frequency for various AC amplitudes (dashed region denotes the area where the applied voltage is limited by the output impedance of the HV interface for safety reasons).

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Application of dielectric spectroscopy for the optimization of high performance liquid crystal mixtures

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The nematic phase of liquid crystal (LC) mixtures is generally used in LC displays. The molecular requirement is the calamitic structure to form the nematic phase. The other properties the molecules need to have depend on the application and function of the liquid crystal display. High performance displays are fast, save energy and show razor sharp images. Materials from Merck make a contribution, which allows these complex demands to be met. So-called reliability issues have to be optimized, which in particular correlate with ionic transport in LCs. For the analysis of the latter (besides standard methods in the LC community), the temperature and frequency dependent dielectric properties as permittivity, conductivity, and dielectric modulus are investigated.

We present typical dielectric spectra for modern LC mixtures, compare them to well-known spectra of simple mixtures in literature (for instance [1]) and highlight the role of different frequency ranges concerning typical mixture characteristics like rotational viscosity that is related to the switching speed in a LCD. We emphasize the importance of dielectric spectroscopy regarding ionic impurities. For this, models (for instance [2, 3]) are applied to the spectra for more detailed analysis of the conductivity contribution.

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Dielectric Spectroscopy and Glass Transitions of Organic Molecules and Mixtures Prepared from Submicron Particle Deposition

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This study presents a new method for collecting and analyzing the dielectric and glass forming properties of small volumes of organic compounds that utilizes a novel nanoparticle deposition technique. A newly developed process was used to generate submicron thin films from nanoparticles through electrostatic precipitation of aerosols onto interdigitated electrodes (IDEs). The thin films of various organic compounds and their mixtures were then analyzed by dielectric spectroscopy as a function of temperature, relative humidity, and chemical composition. The dielectric spectra show that the compounds exhibit super Arrhenius behavior at higher temperatures but maintain only Arrhenius behavior with further cooling. The phase transition between the two Arrhenius behaviors was used to calculate the glass transition temperatures of single organic compounds as well as complex mixtures. These results were compared with the glass transition temperatures derived from other published methods. This collection technique and analysis method may find wide applications especially in the fields of atmospheric sciences and polymer/pharmaceutical industries involving trace amounts of nanoparticles.

Probing the physical state and molecular mobility of naproxen drug confined to nanoporous silica matrices

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The highly crystallizable pharmaceutical drug naproxen was loaded in silica hosts with pores diameter of 2.4, 3.2 and 5.9 nm. To access the guest physical state, DSC, XRD and ATR-FTIR were used. It was found that naproxen is able to crystallize inside pores in the 5.9 nm matrix but becomes full amorphous upon cooling from the melt. Amorphization was successfuly achieved in the 3.2 and 2.4 matrixes. By dielectric spectroscopy a slowing down of the molecular mobility with pore size decreasing was found in coherence with the increase of the glass transition temperature observed by DSC. In amorphous naproxen inside 5.9 nm pores, the dielectric response was deconvoluted in an slow S-process due to molecules interacting with the inner pore wall, and a faster α-relaxation owing to molecules relaxing in the pore core revealing a true confinement effect.

Acknowledgements

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Molecular factors governing the recrystallization of amorphous anti-inflammantory drug in mixtures with small and large excipients

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Transformation of poorly water-soluble crystalline pharmaceuticals to the amorphous form is one of the most promising strategies to improve their oral bioavailability. Unfortunately, the amorphous drugs are usually thermodynamically unstable and may quickly return to their crystalline form. A very promising way to enhance the physical stability of amorphous drugs is to prepare amorphous compositions of active pharmaceutical ingredients (APIs) with certain excipients which can be characterized by significantly different molecular weights, such as polymers, acetate saccharides, and other APIs. By using different experimental techniques (broadband dielectric spectroscopy, differential scanning calorimetry, X-ray diffraction), we examine the effect of adding large molecular weight polymer – polyvinylpyrrolidone (PVP K30) and the small molecular weight excipient – octaacetylmaltose (acMAL) on molecular dynamics as well as the tendency to recrystallization of the amorphous celecoxib (CEL) in the amorphous solid dispersions: CEL-PVP and CEL-acMAL. We found that acMAL is a better inhibitor of recrystallization of amorphous CEL than PVP K30 deep in the glassy state ($T<T_g$). In contrast, PVP K30 is a better crystallization inhibitor of CEL in the supercooled liquid state (at $T>T_g$) than acMal. We compare molecular factors which can govern the recrystallization of amorphous CEL in examined solid dispersions.

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Crystallization of glass-forming liquids studied in T-p space along different iso-invariant lines

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Controlling crystallization and glass-forming tendencies of the molecular liquids is of the great scientific and practical importance. Much about that can be learned from introducing temperature and pressure as thermodynamic control variables. Here we have investigated changes in the crystallization rate along various iso-invariant lines located differently in the two-dimensional T-p phase space. This has included not only isobaric (p=const) or isothermal (T=const) lines, but also temperature and pressure conditions along which the kinetic (τ_α=const) and thermodynamic ($\Delta\mu$=const) driving forces towards crystallization are expected to remain constant. We show that by changing both temperature and pressure one can favor or disfavor crystallization progress. Although the increase of pressure is generally expected to foster the crystallization, while moving along certain iso-lines the crystallization rate can be unaffected (or affected only very slightly) by the pressure/density increase. This includes for example iso-($\Delta\mu$) and iso-(τ_α) lines.

We also found that the thermodynamic driving force towards crystallization is close to being constant when keeping the same τ_α at various thermodynamic conditions. Similarly, we observe that the time scale of the molecular motions changes only very slightly along iso-($\Delta\mu$) line. Our results indicate an intimate link between the kinetic and thermodynamic factors governing the crystallization, and that possibly both cannot be separated neither by changing the temperature nor pressure.

Characterization of the crystalline/amorphous phases of SIMVASTATIN: contribution from TSDC and DRS techniques

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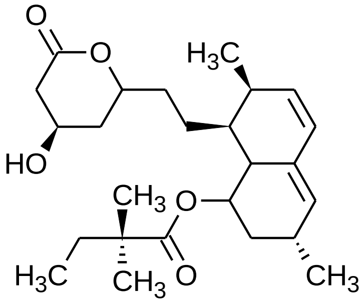

It has been reported that simvastatin (a drug used to reduce the low density lipoprotein cholesterol) presents three crystalline polymorphs with well-defined temperature regions (enantiotropic system). The temperature and enthalpy of these transitions have been determined by differential scanning calorimetry[1,2]: form I is the stable form at room temperature, $T_{melting}$ = 412.2 K, and two low-temperature phases, named as II and III in order of decreasing temperature, occur at $T_{I\rightarrow II}$ = 272 K and $T_{II\rightarrow III}$ = 232 K, respectively.

The main structural difference between the three solid phases was attributed to a conformational disorder of the ester side chain[1,2] and related with variations in the lengths of the hydrogen bonds in the crystal lattice[2], as probed by solid-state NMR[1], single-crystal x-ray diffraction, quantum chemistry calculations and molecular dynamics simulations[2]. Moreover, it has been shown that amorphous simvastatin obtained by the melt-cooling technique presents a high stability relative to recrystallization[3]: solid-state NMR studies revealed a strong dynamic heterogeneity which appears to be essential for the stability of the amorphous form of simvastatin.

The aim of the present study was to investigate the slow molecular motions of this model drug in the different physical states using two complementary dielectric techniques (frequence range ~10^{-3} up to 10^{6} Hz): Dielectric Relaxation Spectroscopy (DRS) and Thermally Stimulated Depolarization Currents (TSDC).

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Universal scaling of dielectric response of various liquid crystals and glass-forming liquids

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New generalized scaling relationship accounting for both the real and imaginary parts of the complex dielectric permittivity data [1,2] will be presented. The generalized scaling procedure has been successfully used for various relaxation processes in numerous liquid crystal materials and glass-forming liquids (hydrogen-bonded and van der Waals) [1,2]. The fact that one obtains common master-curve for relaxations in liquid-like phases (isotropic liquid, cholesteric, nematic, smectic A), solid-like phases (smectic B, conformationally disorder crystal) as well as in supercooled liquid and plastic-crystal phases will be discussed. In supercooled disordered phases the main (alpha) relaxation process is often followed by the beta one or one deals with the excess wing phenomenon [3,4]. As it will be shown the behavior of beta relaxation process and/or excess wing phenomenon is governed by the alpha relaxation process and, moreover, all relaxation curves scaled according to the proposed relation tend to common behavior [2]. What is more, the presented scaling procedure can be applied to NMR data of longitudinal spin-lattice relaxation time, as well as for complex dielelctric modulus, impedance and admittance data.

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Dielectric and ferroelectric behaviour of thin films of trialkylbenzene-1,3,5-tricarboxamide (BTA)

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Trialkylbenzene-1,3,5 tricarboxamides (BTAs)[1] represent a novel class of organic ferroelectric materials, the ferroelectric properties of which rely on a liquid crystalline columnar hexagonal arrangement of H-bonded, stacked polar disc-shaped building blocks. In this work the nature of the polar switching process is investigated by a combination of dielectric relaxation spectroscopy, depth-resolved pyroelectric response measurements, as well as classical frequency- and time-dependent electrical switching experiments. Dielectric spectroscopy revealed several molecular relaxation processes that can be assigned to short columnar reorientation (α-process), collective polarisation inversion in long columns (R-process) as well as a fast, third relaxation mode related to pre-transitional effects[2]. In addition, Curie-Weiss behaviour was found supporting the true ferroelectric nature of the $\mathrm{Col}_{\mathrm{hex}}$-phase. Further experiments were devoted to understand the limited temporal stability of the remnant polarisation at elevated temperatures; here, dielectric measurements under high electric dc-fields confirmed the role of collective H-bonding dynamics in conjunction with amide-flips, which manifests in both a field-dependent dc-conductivity and relaxation strength of the R-process. These results are discussed in terms of switching kinetics as obtained by a rigorous analysis of the ferroelectric hysteresis experiments.

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Remanent polarisation and liquid crystal alignment in composite films of 5CB and 6CB in PVDF-TrFe

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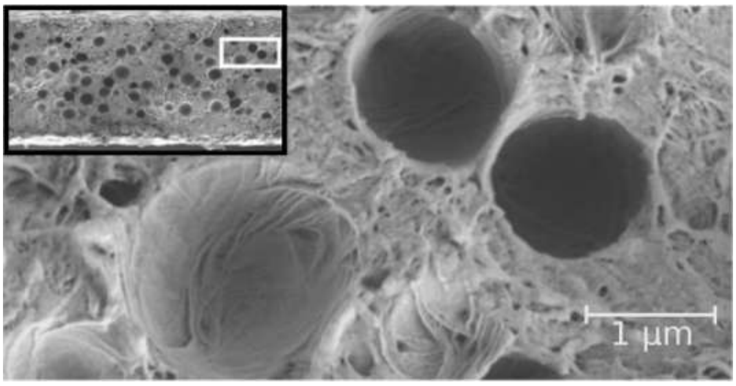
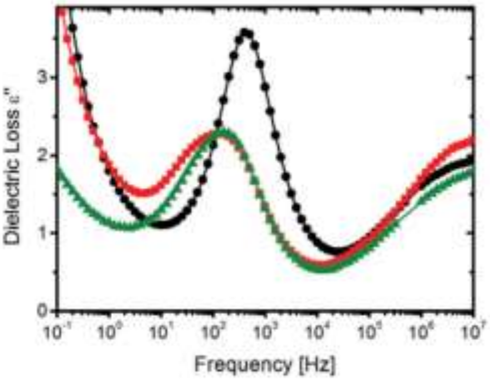
Polymer-dispersed liquid crystals (PDLCs) of ferroelectric poly(vinylidene fluoride-trifluoroethylene) and nematic 4-cyano-4’-n-hexylbiphenyl (6CB) or 4-cyano-4’-n-pentylbiphenyl (5CB) are prepared from solution. After pretreatment the Liquid Crystals (LCs) separate partly from the matrix and aggregate in nearly spherical inclusions (fig. 1). To study the effect of the remanent polarization of the polymer matrix on the polar LCs, their macroscopic alignment is determined by means of Infrared Transition-Moment Orientational Analysis (IR-TMOA). Electric poling at 100 V/µm creates an remanent, ie internal, electric field and causes an increased order parameter of the LCs up to 0.15. After subsequent annealing above the nematic-to-isotropic phase-transition temperature, the order parameter is strongly reduced, but still significantly different from the non-poled film. Both values are 1 to 2 order of magnitude lower than expected from model calculations. Based on dielectric measurements, we attribute this discrepancy to shielding effects of mobile charge carriers at the interface of the LC-inclusions.[1]



Electron micrograph, showing the LC inclusions in the polymer matrix; The framed region in the inset corresponds to the large picture.



Dielectric loss vs frequency of the non-poled (black circles), poled (red squares), and poled and annealed (green triangles) PDLC film.

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Dielectric studies of collagen thin films

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Collagen-based biomaterials gain significant technological interest due to their extraordinary ferroelectric properties [1] and an excellent water binding ability, achieved via the presence of triple helix in the tertiary structure of this protein present in a large number of biological tissues. Dielectric measurements on the dynamics of hydration water in bulk collagen have permitted to highlight the role of the motion of the protein surface in underhydrated conditions[2].

In the form of thin films (thickness of 100 to 1200nm), these materials have already been employed as biocompatible capacitive high accuracy humidity sensors [3]. However, no information on the impact of nanoconfinement on the dynamics of this biomaterial is known.

Here we present the first dielectric measurements on dry collagen thin films prepared by spin casting of solutions of Collagen I from bovine achilles tendon in acetic acid, over broad frequency and temperature ranges. Separation of the electrodes at the nanoscale level, nanocapacitor geometry, facilitated the detection of a weak dipolar dielectric relaxation, otherwise hardly visible in analogous measurents on bulk dry samples. The temperature dependence of the relaxation time of the above mentioned process shows a clear crossover at T_c = 210 K from an Arrhenius behavior at low T to a superArrhenius trend at high T. Remarkably, this process is still active above the melting point of bulk water. The molecular origin of this dielectric relaxation, is discussed in terms of the observed T dependence and of the effect of the amplitude of the E-field on the dynamics.

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Crystallite growth enhances segmental dynamics in star-shaped semi-crystalline polymer

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The impact of nano-scale constraints on the segmental dynamics of polymers is of great interest for fundamental and applied research. On the one hand it is expected to shed light on the still poorly understood principles of the glass transition, on the other hand it is a promising route to develop hybrid materials exhibiting novel properties or enhanced performance. Such a constraint can be achieved e.g. by semi-crystallinity due to nanometer sized crystallites in-between amorphous domains. For isotactic polystyrene (iPS) it is known that the crystallites severely affect the segmental dynamics of adjacent amorphous domains. In case of linear molecules, in those chains which contribute to both crystallites and amorphous regions, the dynamics of connecting segments is slowed down forming a so-called rigid amorphous fraction [1].

In contrast to this established effect, star-shaped iPS with a polyoctahedral silsesquioxane (POSS) molecule as center [2] exhibits strongly enhanced dynamics; the mean relaxation time in the semi-crystalline state is about one decade faster than in the purely amorphous state. A comparison of the relaxation time distribution function of the purely amorphous and semi-crystalline state reveals a considerable fraction of additional faster and extinction of slower relaxation modes in the latter. We assume that the particular architecture of the polymers stabilizes the overall sample volume upon crystallization thus leading to a reduced density in the amorphous domains. Consequently, the segments exhibit faster dynamics which represents a mechanism of thermally induced switching of segmental dynamics.

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Dielectric Investigations of the high Performance Polymer PIM-1 and Nanocomposites containing PhenethylPOSS

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Especially now, in times of the energy revolution, the need for energy efficient separation processes promote the advancement of new high performance materials for use as highly selective separation membranes. Most promising materials in this field, especially for gas separation, are polymers with intrinsic microporosity (PIMs) which were firstly introduced by Budd and McKeown [1]. Currently widespread application of PIMs for membrane technology is still restrained by their strong tendency to physical aging involving a significant loss of their good gas separation properties. This phenomenom is directly related to the molecular mobility. Here for the first time, molecular dynamics and conductivity in PIM-1, the first synthesized PIM, were investigated by broadband dielectric spectroscopy (BDS) [2]. Although an α-relaxation was not observed for PIM-1, as a thermal glass transition temperature has not yet previously been reported below its decomposition temperature at 370°C, surprisingly a conductivity contribution was found which is attributed to intermolecular agglomerates formed by π−π-stacking. Besides the studies on pure PIM-1 a polyhedral oligomeric phenethyl-silsesquioxanes (PhenethylPOSS) was used as nanofiller (0 – 40 wt%) in order to evaluate its ability to improve gas transport properties and probably control physical aging. The molecular mobility of all materials was analyzed by BDS of solution-cast films.

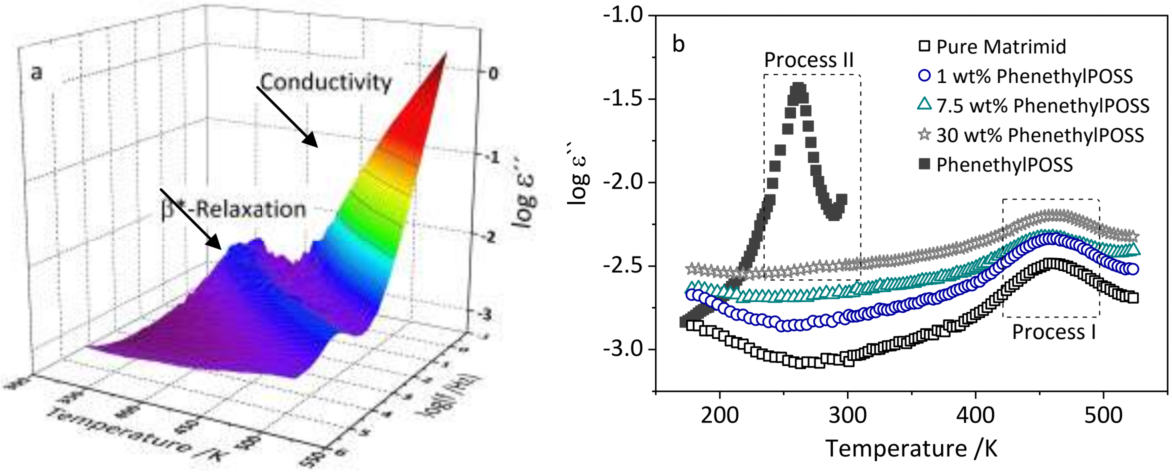

Figure 1: a) 3D representation of the dielectric loss vs. frequency and temperature of PIM-1. b) Dielectric loss vs. temperature of PIM1-PhenethylPOSS composites at a fixed frequency of 1 kHz.

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Behavior of Ultra-Thin Films of Blends of Polystyrene/ Poly(vinyl methyl ether) by Nanosized Relaxation Spectroscopy

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In the course of miniaturizing modern technology down to the molecular scale, understanding the materials behavior has to be investigated and deviations from the bulk that might arises from confinement effects has to be understood. Here, a combination of nano-sized relaxation spectroscopies (Broadband dielectric spectroscopy (BDS) and Specific heat spectroscopy (SHS); employing AC nanochip calorimetry) were utilized to investigate the glassy dynamics of ultra-thin films of blends of Poly (vinyl methyl ether) (PVME) / Polystyrene (PS) 50:50 wt-%, which are miscible bulk (thicknesses: 8nm - 200nm, film thickness was controlled by ellipsometry, film topography by AFM). Both methods are sensitive to different probes; where SHS senses entropy fluctuations while BDS measures dipole fluctuations. For BDS measurements, a recently developed nano-structured electrode sample arrangement is employed; where ultra-thin films are spin-coated on an ultra-flat highly conductive silicon wafer, sandwiched between a wafer with nanostructured SiO_2 nano-spacers with heights between 35 nm and 70 nm. The method was applied for film thicknesses up to 50 nm. For thicker films, the samples were prepared between crossed electrodes. It was proven that, for 50 nm films, both contact methods will lead to identical results. By measuring the dynamic T_g in dependence of the film thickness, SHS showed that the T_g of the whole film was strongly influenced by a nanometer-thick surface layer at the polymer/air interface due to a self-assembling process [1]. The dynamic T_g obtained from the SHS measurements decrease with decreasing film thickness, evidencing the importance of a mobile surface layer at the polymer/air interface for the glass transition of the whole film. Compared to the SHS results, the BDS measurements show a completely different behavior. At high temperatures, the temperature dependence of the relaxation times of the films follows that of bulk-like PS/PVME; obeying the VFT-law. With decreasing temperature, the temperature dependence deviates from the VFT to an Arrhenius law; where the apparent activation energy decreases with decreasing film thickness. This is the first example where confinement induced changes were observed by BDS for ultra-thin films. All results were analyzed in details in a comprehensive discussion.

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Dynamics of asymmetric binary glass formers

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Typical asymmetric binary glass formers are made by polymer-plasticizer systems: A high-T_g polymer is mixed with a low-T_g component, i.e., the components show a high T_g-contrast. Instead, also a non-polymeric high-T_g liquid may be chosen for preparing binary mixtures. We specifically synthesized labeled non-polymeric liquids with T_g > 370 K and M > 1000 g/mol (cf. Fig. 1); as low-T_g component phosphoric esters are employed resulting again in a high T_g-contrast. Such mixed liquids/glasses may be taken as a model for mixtures of large- and small-size molecules investigated also by simulations and mode coupling theory. Applying dielectric spectroscopy and ^{2}H as well as ^{31}P NMR we are able to selectively investigate the component dynamics over the entire concentration range.

As will be demonstrated rather similar dynamics are found in both types of asymmetric mixtures (JCP 140, 094505 & JCP 143, 154506*)*. While qualitatively the dynamics of the high-T_g component does not significantly change in the mixtures, the low-T_g component exhibits fast dynamics in an essentially arrested high-T_g matrix, and quasi-logarithmic correlation functions are identified reflecting pronounced dynamic heterogeneities as a result of intrinsic confinement effects. Two T_g values are extracted, one steadily decreasing with the low-T_g additive concentration, the other exhibiting a maximum (cf. Fig. 1).

Regarding the β–process introduced by the low-T_g component, as in simple liquids it reflects a spatially highly hindered motion with the same activation energy for all contrations and it induces a very similar motion in the high-T_g component, i.e., small molecules “enslave” large molecules (JCP 139, 064508). This may be taken as an indication of the cooperative nature of the β-process.

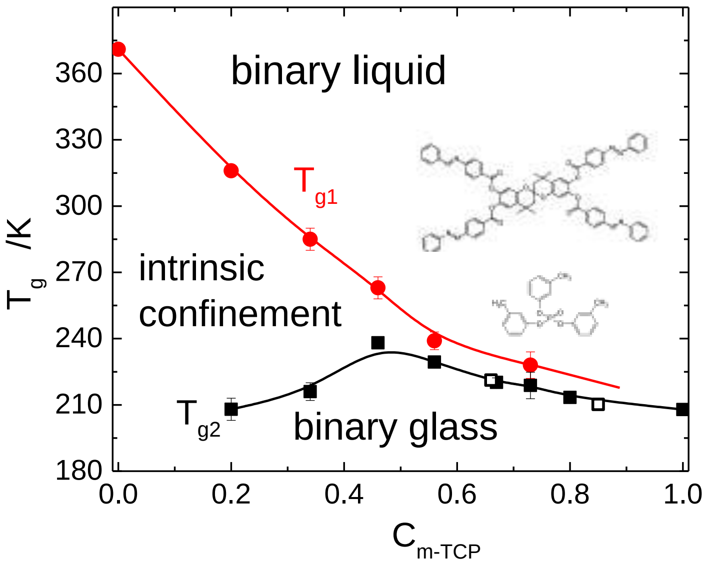

Figure 1. T_g values as a function of concentration in an asymmetric binary glass.

Johari-Goldstein β-relaxation Mistaken for Confinement Effect in Highly Asymmetric Mixtures

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Supported by the primtive relaxation of the Coupling Model, universal existence of a secondary relaxation bearing inseparable relation to the structural α-relaxation is predicted. This prediction has been verified by many experiments in small molecular, metallic, and polymeric glassformers[1] as well as in binary mixtures[2,3] and polymer blends[4]. This special kind of secondary relaxation is named the Johari-Goldstein (JG) β-relaxation to distinguish it from the trivial ones. In highly asymmetric polymer blends, *x*PVME-(1-*x*)PS, where the T_g of the PS component is much higher than PVME, the appearance of a fast process with Arrhenius *T*-dependence in bends with x=0.1 to 0.3 was interpreted initially as local relaxation of PVME *confined* by the glassy matrix of the PS component[5]. Subsequent finding of the α-relaxation of the PVME component by TSDC[6] coexisting at the same temperature with the faster relaxation clearly ruled out the confinement hypothesis in this blend and in another blend, *x*PI-(1-*x*)P*t*BS.[7] We had pointed this out before and also showed[4] from the properties of the fast process that it is actually the JG β-relaxation of the PVME in the blend.

Recntly, Rössler and coworkers[8,9] studied the highly asymmetric mixtures of tripropyl phosphate (TPP) with PS, *x*TPP-(1-x)PS, and mixtures of m-tri-cresyl phosphate (TCP) with a spirobichroman derivative (DH), *x*TCP-(1-*x*)DH. In both studies they found a fast process with Arrhenius *T*-dependence originating from the lower T_g component, TPP or TCP, in mixtures with low values of *x*. This process they interpret as TPP or TCP confined in the rigid glassy matrix of the higher T_g component in the blend, a revival of the old idea.

In this talk we report a critial test of this revived interpretation of the fast Arrhenius process by applying elevated pressure in isothermal and isochronal dielectric measurements. From the response to pressure of the purported confined process expected very different from that of the JG β-relaxation, we can tell which one is the correct interpretation of the data.

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Unraveling Interfacial Dynamics in Polymer Nanocomposites

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It is now well recognized that interfacial layer controls macroscopic properties in polymer nanocomposite (PNC) and in thin polymer films. Polymer structure and dynamics in the interfacial layer are strongly affected by nanoparticles surface. The thickness of this interfacial layer is usually estimated to be several nm. In this talk we overview our recent studies on structure and dynamics of the interfacial layer in various nanocomposite materials [1-5]. Our dielectric relaxation studies and MD-simulations reveal a gradient in the interfacial layer dynamics, but no “glassy” or “dead“ layer [1-3]. Small angle X-ray scattering, DSC and dielectric spectroscopy provide consistent estimates of the interfacial layer thickness in various PNC [1,3-5]. The thickness of the layer increases upon cooling to Tg [3], and depends strongly on polymer rigidity [2], increasing from ~2nm in flexible polymers to ~5 nm in more rigid ones. Detailed studies revealed unexpected molecular weight dependence [4]: a decrease in the interfacial layer thickness and weaker variation in dynamics with increase in chain length. This result contradicts to theoretical predictions and we ascribe it to frustration in chain packing in the interfacial layer that increases with increase in molecular weight [4]. The presented results clearly demonstrate the existence of the interfacial layer with much slower dynamics that propagates a few nm (~2-5 nm) into the polymer matrix. We don't see any signs of the glassy layer as well as any presence of long range (larger than 10nm) effects. At the end, we discuss applicability of these results to thin polymer films and their interfacial layer dynamics.

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Local, global, and particle dynamics in polypropylene glycol / silica nanocomposites.

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The local segmental and global dynamics of polypropylene glycol / silica nanocomposites were studied using rheometry, SANS, and mechanical and dielectric spectroscopies. The particles cause substantial changes in the rheology, including higher and non-Newtonian viscosities. However, no change was observed in the mean relaxation times for either the segmental or normal mode dynamics measured dielectrically. This absence of an effect of the particles is due to masking of the interfacial response by polymer chains remote from the particles. When the unattached polymer was extracted to isolate the interfacial material, very large reductions in both the local and global relaxation times were measured. This speeding up of the dynamics is due in part to the reduced density at the interface, presumably a consequence of poorer packing of tethered chains. In addition, binding of the ether oxygens of the polypropylene glycol truncates the normal mode, which contributes an additional shift of the corresponding relaxation peak to higher frequencies.

At particle concentrations sufficient to cause the viscosity to be shear-rate dependent, the transient viscosity exhibits stress overshoots. If the shear flow is interrupted and then resumed, the magnitude of the overshoot is governed by the quiescent time. Both the time scale of this structural recovery and its temperature-dependence are markedly different from those determined for the chain dynamics. That is, the recovery of the startup transient involves interparticle interactions that are largely decoupled from the local viscosity.

Dielectric Relaxation and Electrical Conductivity of Poly(3-hexyltiophene and its blends with fullerene: from bulk to thin films

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*O*rganics photovoltaics (OPV) is one of the leading technologies aiming to transform solar light into electrical energy. The organic bulk heterojunction (BHJ) is one of the most promising material architectures consisting of an interpenetrating network of an organic donor semiconductor blended with an acceptor one. Blends of poly(3-hexylthiophene) (P3HT), as donor polymer, and a fullerene derivative as acceptor system are among the most promising photovoltaic blends. In this contribution the relaxational behavior and the electrical conductivity of a series of P3HT/phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) blends as revealed by dielectric spectroscopy will be presented. The results show that hexyl lateral chains of the polymer exhibit a low temperature/high frequency relaxation that presents similar features as that observed in polyethylene. This relaxation is not affected by the presence of $PC_{71}BM$ in the blends. Another high temperature/low frequency process associated to electrical conduction is also observed. The dependence with temperature of the electrical conductivity can be separated into two regions. At lower temperature the conductivity exhibits an Arrhenius behavior whereas at high temperature the conductivity can be described by the Gaussian Disorder model. In the low temperature region, the activation energy decreases when increasing the $PC_{71}BM$ content. The electrical conductivity of thin films of P3HT, as revealed by Conducting Atomic Force Microscopy (C-AFM), will be discussed and the effect of surface patterning by means of Laser Induced Periodic Surface Structures (LIPSS) will be described. This method enables the formation of well-ordered ripple nanostructures. C-AFM reveals a higher electrical conduction in the trenches than in the ridges regions. The effect of molecular order on this effect will be further discussed.

Exploring interfacial polarization phenomena in semicrystalline polymer thin films: from local to bulk dielectric measurements

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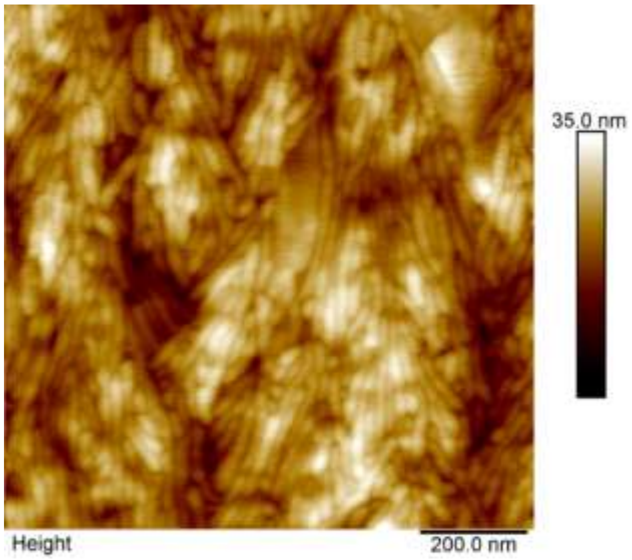
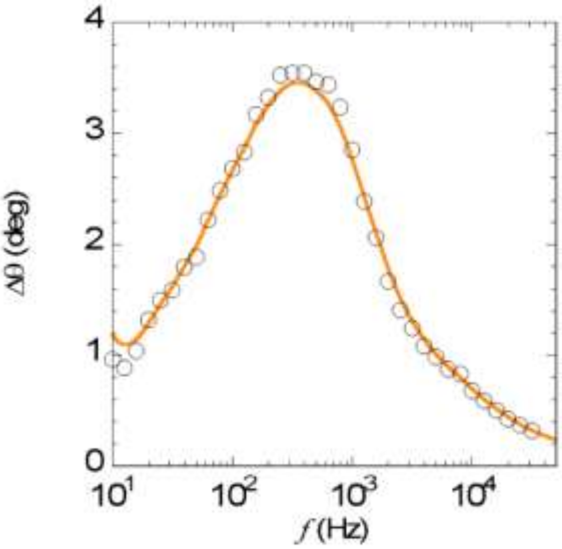
In this work we present the study the interfacial dielectric relaxation, Maxwell-Wagner-Sillars (MWS) polarization, in poly(ethylene oxide) (PEO) films, using microscopic and macroscopic techniques. Considering its high spatial resolution, we have made use of an atomic force microscope (AFM) for performing local dielectric spectroscopy [1,2]. This technique allowed to probe the dielectric response of PEO thin films from 200 nm to 35 nm in thickness, as shown in the figures below. The AFM-based results are analyzed by using a recently published model, linking materials properties and experimental response, in such a way quantitative information is obtained [3]. PEO was furthermore studied in bulk and thin films using standard broadband dielectric spectroscopy and a nanostructured electrode arrangement, respectively. The combination of techniques allowed discussing the *homogenity* of the dielectric response and role played by the crystalline morphology.

AFM Topography



Dielectric response



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Broadband Local Dielectric Spectroscopy

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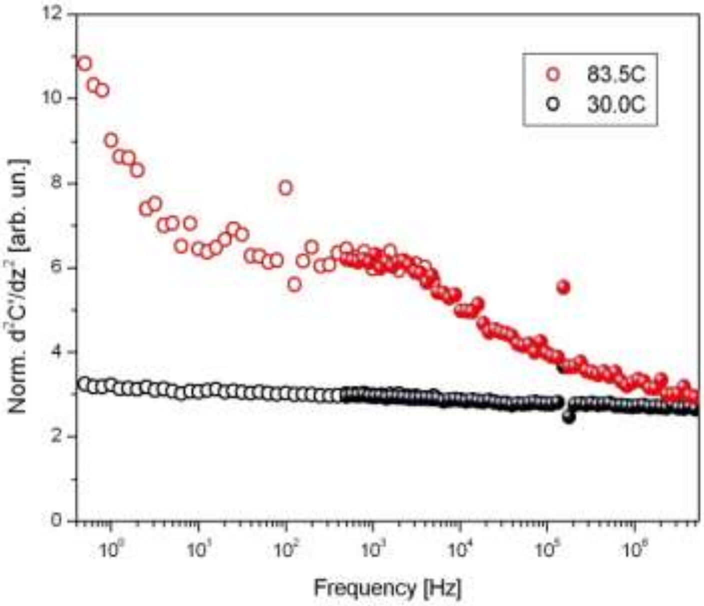
Local dielectric spectroscopy (LDS) [1] is a scanned-probe technique based on atomic force microscopy (AFM), to characterize dynamical response of nanometric portions of a dielectric surface by detecting forces induced by local electrical polarization. LDS can address localized phenomena like those due to surface interactions and confinement in nanostructured [2] and/or ultrathin films [3] and dynamical heterogeneity.[4] Efforts were recently made in the attempt to extend the frequency range of LDS to enlarge its field of applicability as well as to better compare with BDS results. A route to extend the measurement bandwidth of LDS up to the MHz range has been devised in this work [5]. Demonstration on a thin poly (vinyl acetate) film is provided, showing its structural relaxation spectrum on the local scale up to 45°C higher than glass temperature (see figure), and nanoscale resolution dielectric relaxation imaging near conductive nanowires embedded in the polymer matrix was obtained up to 5 MHz frequency, with no physical reason to hinder further bandwidth extension.



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Nanoscale complex impedance and dielectric properties of single CHO cells and E.coli bacteria at GHz frequencies by scanning microwave microscopy

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The application of scanning microwave microscopy (SMM) to extract calibrated electrical properties of single cells and bacteria in air is presented. From the S_{11} images complex impedance and admittance images of Chinese hamster ovary cells and E. coli bacteria deposited on a silicon substrate have been obtained[1]. The broadband capabilities of SMM have been used to characterize the bio-samples between 2GHz and 20GHz. Based on a proposed parallel resistance–capacitance model, the equivalent conductance and parallel capacitance of the cells and bacteria were obtained from the SMM images (Fig. 1). The influence of humidity and frequency on the cell conductance was experimentally studied. Complex impedance images have been analyzed to extract dielectric images of the bacterial cells[2]. Results for single Escherichia coli cells provide a relative electric permittivity of ~4 in dry conditions and ~20 in humid conditions, with no significant loss contributions.

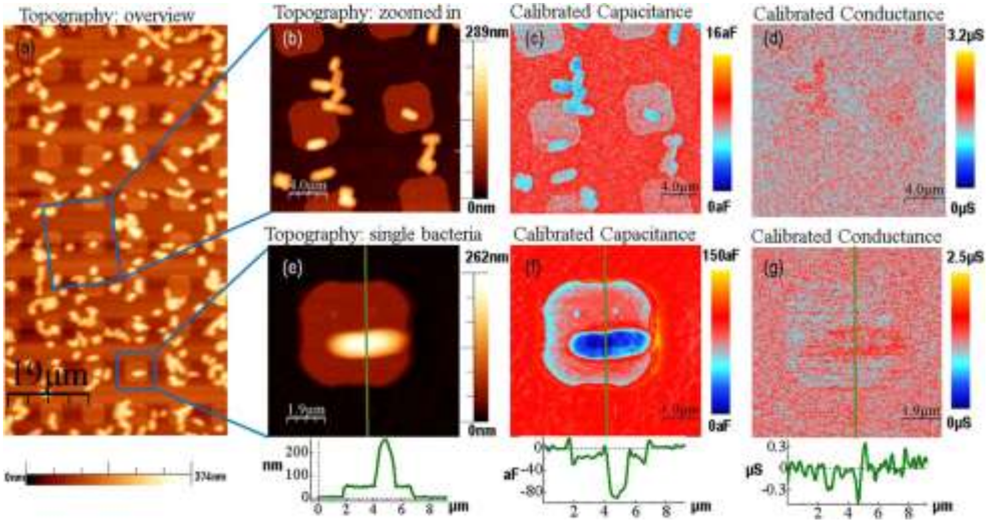

Figure 1. Calibrated complex impedance images of bacteria in air at 19.9 GHz. SMM Topography image with bacteria on top of Si++ substrate with SiO2 pillars is shown in (a) (b) (e). (c) and (f) are calibrated capacitance images at two positions. Images (d) and (g) show calibrated conductance images at the two positions. Cross-sections presented below (e)–(g) are taken as indicated in images.

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Water contribution to the dielectric spectra of electrolytes and proteins

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Dielectric spectroscopy is an important tool to study structural and dynamical properties of electrolyte and protein solutions, since spectral features at different frequencies address competing processes in a vast range of time scales. We discuss several dielectric modes that arise from the dielectric response of peptides, counterions and water molecules.

Solvation water in electrolyte solution constitutes without doubt the simplest scenario, yet a number of open and puzzling questions exist. Infra-red spectroscopic studies demonstrate that solvation water next to ions is generally slowed down in its orientational motion. In contrast, experiments in the GHz and the THz regimes probe the collective water motion and demonstrate a speed-up (blue-shift) of the water relaxation with rising electrolyte concentration. This blue shift is due to collective dynamic effects, i.e., the coupling of the dynamics of one water molecule to its neighbors. The dielectric decrement and the blue shift of electrolyte dielectric spectra are connected and the consequence of the dielectric structure breaking influence of ions on the first solvation shell of water, in line with the Madden−Kivelson theory.

Simulations also yield insights into the dynamic coupling between peptide motion and the surrounding water shell: while the polarization correlations between hydration water molecules themselves pick up a weak feature in the sub-GHz frequency range characteristic of the peptide relaxation mode, the peptide-peptide polarization shows no signal in the 10 GHz range, where bulk water polarizations relax. In connection to the literature debate on whether hydration water is slaved by the peptide dynamics or whether it slaves peptide dynamics, we find no sign of the peptide acquiring any traces of fast water polarization dynamics.

Microwave dielectric spectroscopy of alive single human cells

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Dielectric spectroscopy is a powerful technique for non-ionizing and non-destructive material characterization. Therefore, its development for the analysis of living cells is very attractive for biological researches and biomedical applications, where non-invasivity, label-free and contact-less abilities as well as in-liquid measurements constitute important leitmotivs. Additionnaly, the investigation of the microwave band for dielectric spectroscopy enables the measurements of living cells directly into their culture medium, without tremendous losses induced by the rich ionic and nutrients content of the surrounding fluid [1]. This ability should be considered in complementarity to the electromagnetic field penetration beyond the capacitive bi-lipid cytoplasmic membrane of cells in this frequency range and consequently confers a strong interest to develop and evaluate microwave dielectric spectroscopy for cellular analysis.

Demonstrations of microwave dielectric spectroscopy have been performed with cells suspensions [1] and also at the single cell level in different measurement conditions [2-4].

In our developments, we have developed a microwave based sensor able to trap a single cell surrounded by its culture medium (traditional RMPI medium with 10% of Foetal Calf Serum) [5]. In this paper, we focus on the broadband capacitive and conductive contrasts from 40 MHz to 40 GHz, which have been successfully measured on several individual living and dead cancer cells (THP1 cell lines). Microwave dielectric spectroscopy of single cells confirms the results previously obtained for cells suspensions [6]. Dead cells present indeed an increased capacitive contrast compared to living ones, induced by the equilibrium between intra and extracellular media, due to the permeabilization of the plasma membrane. This result is corroborated by the real time monitoring of a chemically induced cell death with microwave dielectric spectroscopy, performed at the single cell level. It not only enables to extract dielectric spectra of the same single cell in its two pathological states, alive and dead, but it also provides the death kinetic of the single cell submitted to a specific chemical and its associated dose. It opens the door toward dielectric kinetic investigations of chemical impacts on single cells, with potential applications in personalized medicine.

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Dynamics of Water Molecules Absorbed into Stratum Corneum

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When water is confined or absorbed into some complex matrices, its physical properties are significantly changed from bulk water due to perturbations from the matrices interfaces. Specifically, dynamic properties of water can be elucidated via dielectric spectroscopy (DS) and thereby the interfacial effects between water molecules and the matrices can be clarified. Stratum corneum (SC), which is the outermost layer of skin, has a high capability to absorb water and provides complex interfacial effects on the physical properties of water. These effects most likely play important roles on moisturization, preservation, and treatment of skin.

In the present study, dielectric spectra of SC have been measured at low temperatures. At a high hydration level, several dielectric processes, middle frequency (M) process and bimodal (B1 and B2) process, were observed at a quenched condition whereas high frequency (H) process was additionally recognized at a slow cooled condition. We attribute them to the dynamics of water at different conditions. Comparison with the literature data reveals that the M process shares similar temperature dependence with dielectric process commonly reported in a variety of hydrated hydrophilic matrices, such as proteins. Thus, we identify the M process to the common dielectric process reflecting dynamics of hydration water. With the aid of many literatures on static structures of ice, we suggest that the cubic ice (Ic) phase dominantly appears in this system in the case of quench while the ordinal hexagonal ice (Ih) phase is grown in the case of slow cooling. Comparing between quenched and slow cooled spectra and literature data, we attribute the B1 and B2 process to water molecular dynamics in ice Ic and H process to that in ice Ih. As a conclusion, our assignments on dielectric processes to the dynamics of water molecules at different conditions should open the possibility that water at different states can be discerned each other via DS.

Effect of Compression on the Ion Conduction in Polymerized Ionic Liquid

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Polymerized ionic liquids (poly-ILs) are a special class of ionic conductors formed by the mobile cations or anions and the repeating counterionic species covalently bonded to the polymer backbone. Due to the combination of the unique properties of ionic liquids with macromolecular architecture of polymers, poly-ILs have become the attractive candidates for potential applications in energy storage and electrochemical devices.

In this talk we examine the relation between charge transport and segmental dynamics in several protic and aprotic polymerized imidazolium-based ionic liquids in the temperature and pressure thermodynamic space. The results of ambient pressure dielectric experiments combined with temperature-modulated differential scanning calorimetry measurements have revealed a significant separation between the time scale of charge and mass transport in all examined systems. However, squeezing of the studied materials brings the opposite effect on the ions dynamics in protic and aprotic polymerized ionic liquids. We have found that the decoupling between τ_σ and τ_α is reduced under conditions of high compression for aprotic polyILs that is attributed to significant slowing down in anions mobility. On the other hand, the time scale separation between charge transport and segmental dynamics is much more pronounced for protic ionic polymers that provides a proof of fast proton hopping in these systems. The analysis of dielectric data involving activation energy, activation volume and dT_g/dP coeficients provide a fundamental understanding of the ion transport properties in polymerized ionic systems used for diverse emerging technologies.

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Ionic relaxation process connecting both local and macroscopic charge dynamics in conducting materials

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Understanding the microscopic mechanisms of charge migration is the key for any rational design of electrochemical devices with large storage and transport capabilities. Accessing charge fluctuations in a wide dynamic range, dielectric spectroscopy is the workhorse technique covering both the subdiffusive and the diffusive regimes of charge carriers [1]. Usually, the response of conducting materials is discussed in the literature in terms of conductivity spectra. Only little attention is paid to the relaxation process that marks the crossover between the two transport regimes and that is revealed only in the permittivity representation of the dielectric data. This relaxation feature is not related to a reorientation process of permanent dipole moments and it occurs in a wide variety of materials with both high and low ion concentration, including ionic liquids, polymerized ionic liquids, glassy and crystalline conductors, and polymer electrolytes. Moreover, recent studies [2,3] demonstrated that popular theoretical approaches, including the Random Barrier Model [4], are not able to describe its salient features, although these models provide a perfect description of the conductivity spectra in these materials. In this presentation we will provide evidence that this universal relaxation process contains essential information such as the effective number of charge carriers, the volume of local Coulombic interactions, and the spatial onset of random-walk charge dynamics. Additionally, a new phenomenological approach will be introduced which is able to access diffusivity of charge carriers from the characteristic time scale of the relaxation process, without any adjustable parameters.

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Molecular dynamics, charge transport and mesoscopic structure in Polymeric Ionic Liquids (PILs)

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While glassy dynamics and charge transport coincide in low-molecular weight Ionic Liquids (ILs), Polymeric Ionic Liquids (PILs) are characterized by the decoupling between them. This effect is so far most strongly pronounced for the investigated homologous series of 16 Polyisobutylene (PIB)-based PILs. By systematically varying the cationic IL-like headgroups, counteranions and molecular weights, it is possible to analyze electrode polarization, molecular dynamics and charge transport, as well as the mesoscopic structure by means of BDS in a temperature range between 200 and 400 K and a frequency window of 1E-2 - 1E7 Hz. The latter one presenting the microphase-separated character of the PILs under study can be quantitatively described within the framework of an effective medium approximation (EMA) reflecting high conductive IL-like micelles embedded in a high resistive polymeric matrix.

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Conductivity and relaxation dynamics of ionic liquids[a]

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Finding new materials to improve energy-storage devices is an important topic in materials science. For example, liquid electrolytes, as a functional part of supercapacitors and batteries, bear a huge potential for advances. Salts that are liquid at ambient temperatures - so-called ionic liquids - are promising candidates to enhance security and chemical stability [1]. However, concerning the ionic conductivity, a key-factor for these devices, ionic liquids still do not reach the performance of conventional electrolytes. As ionic liquids are composed of large non-symmetrical organic cations and weakly coordinating anions, there is a huge number of possible combinations to design an electrolyte with the required ionic conductivity. To reach this goal, a better understanding of the underlying microscopic mechanisms is necessary [2].

Dielectric spectroscopy is a powerful tool for investigating the microscopic motions of dipolar molecules and the ionic conductivity in ionic liquids. We present dielectric results on a large variety of these liquids in a broad temperature and frequency range. All studied systems show dynamic properties typical for glassy matter and their glass temperature, as well as the so-called fragility, determine their room-temperature ionic conductivity [3]. The latter quantity characterizes the non-canonical super-Arrhenius temperature dependence of their ionic mobility. The spectra of ionic liquids reveal strong electrode polarization that is driven by their ionic conductivity. To gain a deeper understanding on a molecular level, we access the intrinsic properties using an equivalent circuit approach [4]. This enables the unequivocal determination of the relaxation times of the involved dynamic processes. The primary relaxation can be attributed to the reorientational motion of the cations and we discuss if it can be regarded as a structural relaxation. A secondary relaxation, often present in these liquids can be interpreted as a Johari-Goldstein β relaxation [5]. By analyzing these glassy dynamics we aim to gain insight into the underlying mechanism of the conductivity to pave a way for new ionic liquids with enhanced conductivity.

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The ionic liquid gating process of YBCO EDLT probed by Dielectric Spectroscopy

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Double Layer Transistors (EDLT) are becoming a popular tool for inducing novel phases in correlated materials. In this configuration the bias voltage is applied at a gate and traslated via an ionic liquid to the surface of the material under study, producing a large electrostatic doping with carrier densities up to $5*10^{14}cm^{-2}$, 50 times larger than the limit of devices with solid insulator in the gate [1-3].

In this work we present a characterization of the ionic liquid mostly used in these experiments, the N,N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis-(trifluoro-methylsulfonyl)imide (DEME-TFSI) by means of dielectric spectroscopy. Both the intrinsic behavior and “in operando” response are probed. An EDLT formed by a thin film of the high temperature superconducting cuprate $YBa_2Cu_3O_{7-d}$ (YBCO) and the DEME TFSI ionic liquid shows the different regimes corresponding to the bulk ionic liquid behavior and the the charge accumulation at the gating electrode. The presence of electroquemical reactions at the different gating voltages in the YBCO surface will be analized.

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Proton Transport in Imidazoles: Unraveling the Role of Supramolecular Structure

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Supramolecular hydrogen bonded structures are found in a wide variety of materials such as hydrogen-bonding liquids, ionic liquids, copolymers, proteins, and organic ferroelectrics. [1-4] A detailed quantitative understanding of the impact of such extended structures on resultant physicochemical properties is vital for technologies in which these advanced materials are employed. Imidazoles are a class of widely available hydrogen-bonded materials which are capable of forming supramolecular hydrogen-bonded assemblies. In this talk, studies of glass-forming imidazoles and their mixtures with small amounts of additives over wide temperature ranges using broadband dielectric spectroscopy, Fourier transform infrared spectroscopy, depolarized dynamic light scattering, viscometry, and calorimetry will be presented. It is found that minute amounts of proton donors completely disrupt the supramolecular H-bonded chains, indicated by the disappearance of the slow Debye-like relaxations.[4] The supramolecular networks remain unaltered, with the exception of plasticizer effects, when other diluents devoid of proton donors are used. These changes in the size and nature of the hydrogen bonded networks have significant effects on proton transport and dynamics in these materials. In this talk, detailed studies enabling the correlation between supramolecular hydrogen bonding, structural dynamics and proton transfer in these materials will be discussed.

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Electrical Mobility of Lithium ions in Boro-germano-phosphate Glasses

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Lithium ion mobility upon addition of germanium oxide in the two series of mixed glass former lithium phosphate and boro-phosphate glasses has been investigated. The electrical conductivity of the ternary mixed glass former $40Li_2O$-$(60\text{-}x)P_2O_5$-$xGeO_2$ glasses as well as quaternary $40Li_2O$–$10B_2O_3$–$(50\text{-}x)P_2O_5$–$xGeO_2$, glasses with 0 to 25 mol% GeO_2 have been carried out over a wide range of temperatures (183 to 523 K) and frequencies (0.01 Hz to 1 MHz).[1,2] The observed changes in dc conductivity due to the addition of GeO_2 at constant lithium ion concentration is attributed to the reorganization of the glass network. In this talk, both structure and electrical/dielectric properties of these glass systems and their dependence on GeO_2 content will be reported. Structure of these glasses was studied by ^{31}P and ^{11}B MAS NMR spectroscopy and Raman spectroscopy. ^{31}P MAS NMR and Raman spectra reflect the depolymerization of phosphate chains by the incorporation of GeO_n polyhedra. In addition, ^{11}B MAS NMR spectra in boro-phosphate glasses reveal the formation of mixed structural units $B(OP)_3(OGe)$ and further, a decomposition of the ^{11}B MAS NMR spectra gives quantitative measure on the number of BO_3 and $B(OP)_3(OGe)$ structural units.[1] This structural analysis has been combined with impedance measurements and modeling to develop understanding of the role of GeO_2 addition on the lithium ion mobility.

The increase in dc conductivity with addition of GeO_2 is attributed to the formation of ion conducting channels arising from the structural modification and formation of the P-O-Ge linkages, resulting in an easy migration of Li^+ ions along these bonds. At higher GeO_2 content, the glass network is found to be more densely packed which increases its anionic character, and hence results in a slight decrease in the mobility of Li^+ ions. The MIGRATION concept was used to calculate the spatial extent of localized diffusion of Li^+ ions around the network[3], yielding a more complete picture about transport in these two glass systems.

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Contribution of the dielectric spectroscopy to the multiscale study of the electrode materials

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The improvement of battery performance requires the rationale optimization of the composite electrode. The developments of new experimental techniques as well as methodologies are needed to understand the relationships between the composition, the architecture and the performance of composite electrodes. The fruitful contribution of Broadband Dielectric Spectroscopy (BDS) to study hierarchical materials applied to lithium ion and lithium metal batteries electrodes have been previously shown [1-4]. The results demonstrate that the broadband dielectric spectroscopy technique is very sensitive to the different scales of the electrode architecture involved in the electronic transport, from interatomic distances to macroscopic sizes, as well as to the morphology at these scales, coarse or fine distribution of the constituents. When the frequency increases, different kinds of polarizations appear from macroscopic sizes to interatomic distances and give rise to dielectric relaxations in the following order: (a) space-charge polarization (low-frequency range) due to the interface sample/current collector; (b) polarization of clusters (or agglomerates) of particles (micronic scale); (c) polarization of particles due to the existence of resistive junctions between them; (d) electronic transfers (at nanometric or at interatomic scale). The BDS measurement was up to now ex situ measurement, on dry electrode. They provide a fundamental insight into the conduction properties at all scales of the materials before being integrated in a real battery. An innovative device (measurement cell) has been developed to make synchronized BDS measurements and electrochemical cycling: the frequency range is about 10^2 - 10^{10} Hz. In this work, data acquisitions were made on dry electrodes (Active material / Carbon black / PVdF) and then on the same electrode wetted with an electrolyte. Short- and long-range motions of ions are evidenced in the low-frequency region. At higher frequencies, the study shows for the first time the influence of the ions of the electrolyte on the transfer of the electronic charges (and conversely) at the micronic and nanometric scales [4]. The new device opens thus important prospects to determine the evolutions of the multi-scales electrical properties during electrochemical cycling.

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Li^+ Transference Numbers in Liquid Battery Electrolytes obtained by Very-low-frequency Impedance Spectroscopy

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Liquid electrolytes based on carbonates, glymes and ionic liquids (IL) are of considerable interest for various applications in electrochemistry, *e.g.* for electrodeposition, for corrosion inhibition, for supercapacitors, for dye-sensitized solar cells and for lithium-ion batteries. In the case of lithium-ion batteries, the transport properties of Li^+ ions under the influence of electric potential gradients and concentration gradients play an important role for the battery performance. In order to assess these transport properties, transport numbers and transference numbers of Li^+ ions have been measured by means of various experimental techniques, such as pulsed field gradient NMR (PFG-NMR) and potentiostatic polarization techniques [1]. For ideal electrolytes, transference and transport numbers are identical. However, this is not the case for concentrated battery electrolytes. Consequently, ion transport limitations in batteries cannot be predicted exclusively from transport numbers obtained by PFG-NMR.

We have measured the Li^+ transference numbers of different liquid battery electrolytes by means of very-low-frequency impedance spectroscopy (VLF-IS) at variable spacing between Li electrodes [2]. Our results show that the Li^+ transference numbers of the standard electrolyte LP30 and of a 1-1 mixture of tetraglyme (G4) with LiTFSI are much smaller than the Li^+ transport numbers $t_{\mathrm{Li}^+}^{\mathrm{NMR}}$ obtained from pulsed-field gradient NMR measurements. On the other hand, in the case of an ionic liquid-based electrolyte, the values for $t_{\mathrm{Li}^+}^{\mathrm{current}}$ and $t_{\mathrm{Li}^+}^{\mathrm{NMR}}$ are more similar. In order to rationalize the large differences between $t_{\mathrm{Li}^+}^{\mathrm{current}}$ and $t_{\mathrm{Li}^+}^{\mathrm{NMR}}$ found for LP30 and G4/ Li-TFSI, we combine the Onsager reciprocal relations with linear response theory, and we derive expressions for $t_{\mathrm{Li}^+}^{\mathrm{current}}$, which take into account all correlations between ionic movements in the electrolyte. Thereby we show that $t_{\mathrm{Li}^+}^{\mathrm{current}}$ can be much considerably smaller than $t_{\mathrm{Li}^+}^{\mathrm{NMR}}$, if strong directional correlations exist between the movements of cations and anions. Finally, we discuss differences in Li^+ transference numbers obtained by VLF-IS and by potentiostatic polarization measurements.

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Deviation from Scaling Law and Excess Dielectric Loss in Mixed Alkali Glasses

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Ionic conductivity of mixed alkali glasses exhibits strong minimum at intermediate compositions, which is well known as a "mixed alkali effect (MAE)". The origin of the MAE is well explained by a dynamic structure model (DSM) considering a percolation pathway and dynamic site-mismmatch effect [1]. The frequency dependence of the ionic conductivity in the mixed alkali region is different from those in single alkali glasses ex. skews in impedance spectra [2], which was also discussed in view of scaling concept [3] and MIGRATION model[4] etc.

We have remeasured the dielectric response of 20[(1-x)Li_2O-xNa_2O]-80B_2O_3 glasses in frequency range from 0.1Hz to 1MHz and analyzed by scaling equations.

Although the temperature scaling is very well fitted, a considerable deviation is seen in the midle frequency region (Fig. 1),which is also seen in the real part of dielectric function (Fig. 2), which is well fitted by the equation (1).

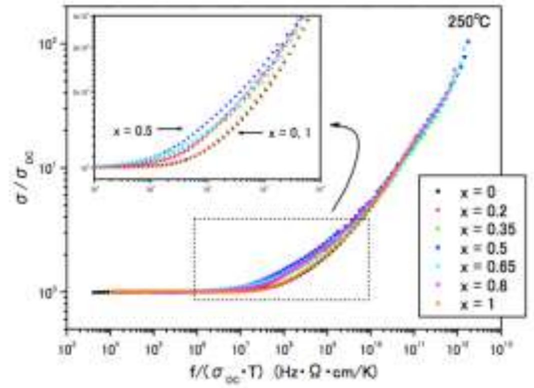

Fig.1 Conductivity scaling on 20[(1-x)Li_2O-xNa_2O]-80B_2O_3 glasses.

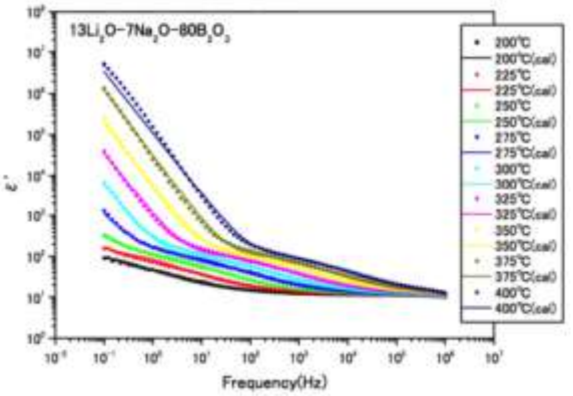

Fig.2 Permittivity of 0.13Li_2O-0.7Na_2O-0.8B_2O_3 glass.

$$\varepsilon^{*}_{obs} = C_{if}\omega^{if} + \frac{\sigma_0}{i\omega} + \frac{\Delta\varepsilon}{\left[1+(i\omega\tau)^n\right]^m} + \varepsilon_{\infty} \tag{1}$$

The extra dielectric loss component Δε shows a maximum at x=0.5, where the conductivity shows minimum. Based on the frequency sum rule, this extra loss can be attributed to the back-and-forth motion of the locally caged ions by surrounding other ions as modeled in the DSM.

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Generalized Theory of Dielectric Response in Disordered Media with Heterogeneities on Multiple Spatial Scales

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Dielectric relaxation spectra of most molecular liquids and polymer melts are asymmetrically broadened. Many theoretical explanations invoke distributions of relaxation times or cooperatively rearrangeing volumes. A common feature is the emergence of measure valued functions from subscale heterogeneities. The novel systematic scaling approach to macroscopic heterogeneity introduced in this presentatio is based on position dependent limiting local porosity distributions. Limiting local porosity distributions were originally introduced to replace pore size distributions and are found here to be of much wider significance. They are related to parametrized measures of weakly convergent sequences of nonrandom functions of position. The frequency dependent complex dielectric function for media with position dependent heterogeneities on multiple length scales is then related to distributions of local volume fractions in a quasistatic and selfconsistent approximation. The approach separates scales by scale factor functions of regular variation in the scaling limit.

Complex Current Analysis for the Description of Combined Conduction and Dielectric Relaxation Processes in Solids

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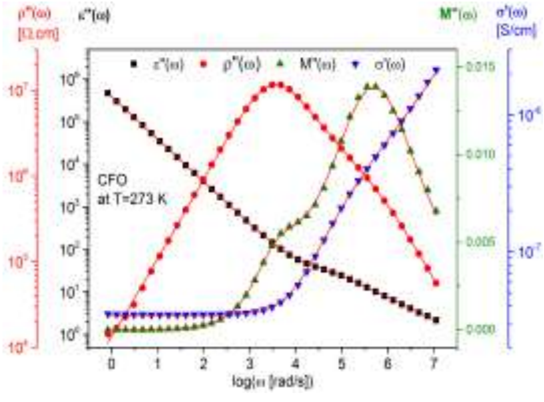
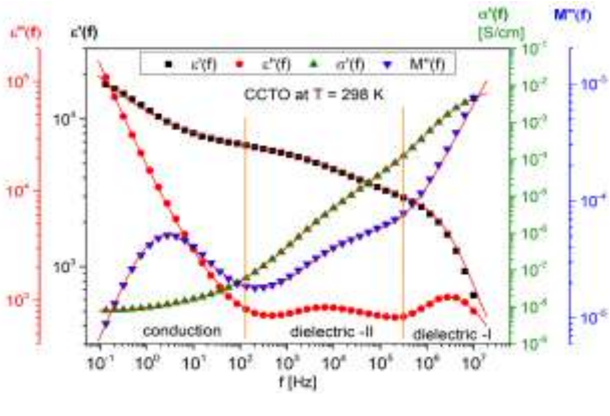
Impedance/dielectric spectroscope generally measures complex current $I^*(\omega)$ and we use various representations like, $Z^*(\omega)$, $\varepsilon^*(\omega)$, $\sigma^*(\omega)$ and $M^*(\omega)$ to study the electrical properties. Materials possessing both conductive and dielectric relaxations have different fit parameters in different representations, since we do not have a proper approach to combine these relaxation processes. Conduction and dielectric relaxation are linked to Jonscher's idea of 'pinned dipole' and 'free dipole' relaxations. Combined Cole-Cole type 'pinned dipole' with conduction relaxation time τ_c and 'free dipole' with dielectric relaxation time τ_d is formulated. The complex current density of the combined processes are found to be $\mathbf{J}^*_{tot}(\omega,t)=\sigma_c^*(\omega)\mathbf{E}(\omega,t)+\varepsilon_0\varepsilon_d^*(\omega)\partial\mathbf{E}(\omega,t)/\partial t$, where $\sigma_c^*(\omega)$ and $\varepsilon_d^*(\omega)$ are the complex conductivity due to 'pinned dipole' and complex permittivity of 'free dipole' respectively. We obtained total complex current density as $\mathbf{J}^*_{tot}(\omega,t)=\sigma_{tot}^*(\omega)\mathbf{E}(\omega,t)$, where $\sigma^*_{tot}(\omega)=\sigma_c^*(\omega)+i\omega\varepsilon_d^*(\omega)$.

The combined Cole-Cole type 'pinned dipole' and 'free dipole' have total complex conductivity, $\sigma_{tot}^*(\omega)=\sigma_c+\sigma_c(i\omega\tau_c)^{\alpha c}+i\omega\varepsilon_0(\Delta\varepsilon_d/(1+(i\omega\tau_d)^{\alpha d})+\varepsilon_\infty)$. The impedance data of various systems like $Mn_{0.5}Zn_{0.5}Fe_2O_4$, $CoFe_2O_4$, $SrFe_{12}O_{19}$, $LiCoO_2$, $CaCu_3Ti_4O_{12}$ and $Na_{1.2}K_{1.8}Al_2P_3O_{12}$ are analysed and results are shown in four different electrical representations in figures below in terms of relaxation times τ_c and τ_d. The measured complex current data analyses with 'pinned dipole' and 'free dipole' processes show representation independent fit parameters. The coupled/decoupled behaviour of 'pinned dipole' and 'free dipole' are discussed in terms of relaxation times τ_c and τ_d in the present work.





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Electrode polarization vs. Maxwell-Wagner-Sillars interfacial polarization: what is similar, what is different, applications

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The phenomenon of electrical polarization is omnipresent—under a variety of different forms—in the dielectric spectra of materials. It covers a broad range of physical phenomena as different as electronic and atomic polarization, orientation polarization of permanent dipole moments, Maxwell-Wagner-Sillars interfacial polarization, electrode polarization. In the dielectric spectra characterizing the electrical and dielectric properties of materials, all these physical processes give rise to specific dielectric dispersions manifested in specific frequency ranges. Being similar in their nature, different forms of electrical polarization can be expected to show, to a certain extent, similar scaling laws. This expectation is indeed confirmed by the results reported in the literature. It has been recently shown, for instance, that some scaling laws governing the characteristic frequencies of interfacial polarization effects in composite materials with spherical fillers are identical to the scaling laws of electrode polarization effects [1]. But more important than analyzing the similarities between different forms of electrical polarization is to understand in which aspects they could be fundamentally different. This would give one a powerful means to discriminate between different contributions arising in the dielectric spectra of materials, which could be of significant importance in the case of samples showing a complex dielectric behavior.

In the present contribution, the scaling laws corresponding to two different manifestations of the phenomenon of electrical polarization (electrode polarization and Maxwell-Wagner-Sillars interfacial polarization) were determined and systematically analyzed and compared [2]. To this purpose, dielectric measurements by Broadband Dielectric Spectroscopy on ionic liquids and on polymer bi-layers as well as numerical and analytical calculations have been carried out. It is shown that, to a large extent, identical scaling laws can be derived for these two dielectric phenomena taking place at external and internal interfaces. Surprisingly, a fundamentally different behavior concerning the interrelation between the characteristic frequencies is found. This brings direct evidence that different manifestations of the phenomenon of electrical polarization can be discriminated by examining the inter-relation governing their characteristic frequencies. Our study will furthermore demonstrate several applications of these two electrical polarization phenomena.

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Ageing of electrochromic tungsten oxide thin films studied by impedance spectroscopy

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Tungsten oxide is the most widely used cathodic electrochromic material for smart window applications and a major challenge is to ensure the durability over a service life of more than 20 years. Hence, the degradation under operating conditions must be better understood and preferably prevented. Recent progress in this field includes studies of the power-law kinetics of the degradation process [1] as well as the possibility to rejuvenate degraded films, thereby restoring them to their initial state [2]. In this paper we use impedance spectroscopy to investigate electrochemical ageing of sputter deposited tungsten oxide thin films. Impedance spectroscopy measurements were carried out in a Li+-containing electrolyte, from the open circuit potential at about 3.2V vs. Li down to (1) 2.2 V, which is in the reversible intercalation range; (2) 1.5 V and (3) 1.0 V; at these latter voltages Li intercalation has been found to be irreversible. Subsequently, measurements were carried out for increasing voltages up to the starting point at 3.2 V vs. Li. The intercalated charge capacity was unaffected when potentials below 2.0 V were avoided, while it decreased drastically on the return path from 1.5 V and 1.0 V vs. Li. We interpret this ageing behaviour as an effect of trapping of Li ions irreversibly in the film. Secondly, after the films had been subjected to the low potentials known to induce degradation, the charge transfer resistance in the usual operating range above 2.0 V vs. Li showed a marked increase. This is interpreted as a signature of the development of a solid-electrolyte interface. In conclusion, our measurements suggest that the development of the solid-electrolyte interface may be responsible for the slow degradation observed under normal operating conditions, while Li ion trapping is mainly responsible for severe degradation at potentials significantly below 2.0 V vs. Li.

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Poster contributions

Dielectric relaxation time of ice Ih in partially crystallized aqueous polymer mixtures

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Dielectric relaxation of ice-Ih has been investigated by many researchers. Pioneering studies focused on the temperature dependence of the dielectric relaxation time, τ_{ice}, were reported by Auty in 1952[1] and Johari in 1981[2]. However, the temperature dependences of τ_{ice} found in these studies are not in agreement. While Auty et al. reported a single Arrhenius temperature dependence of τ_{ice} for the entire 207–273 K temperature range, Johari et al. reported changes in the temperature dependence of τ_{ice} at 230 and 140 K. Recently, we found that τ_{ice} can be controlled by preparing method. Temperature dependence of τ_{ice} with rapid crystallization shows the same properties at temperatures down to 140 K as that reported by Johari et al. On the other hand, ice obtained by slow crystallization exhibits the same temperature dependence of τ_{ice} as those reported by Auty et al.[3]

τ_{ice} in partially crystallized aqueous protein mixtures has also been investigated.[4,5] According to literatures results, τ_{ice} in partially crystallized aqueous mixtures seems to be classified into Johari[5] or Auty[4] type. In order to discover classification of τ_{ice}, in this study, τ_{ice} in partially crystallized gelatin and poly (vinyl pyrrolidone) aqueous mixtures with low polymer concentration (1-5 wt%) have investigated. Figure shows relaxation map for τ_{ice} of pure and in partially crystallized gelatin-water mixtures (1, 3, 5 wt%). τ_{ice} in the mixtures change from Johari[2] to Auty[1] type with increasing gelatin concentration. It implies that the temperature dependence of τ_{ice} is controlled by microscopic viscoelastic property.

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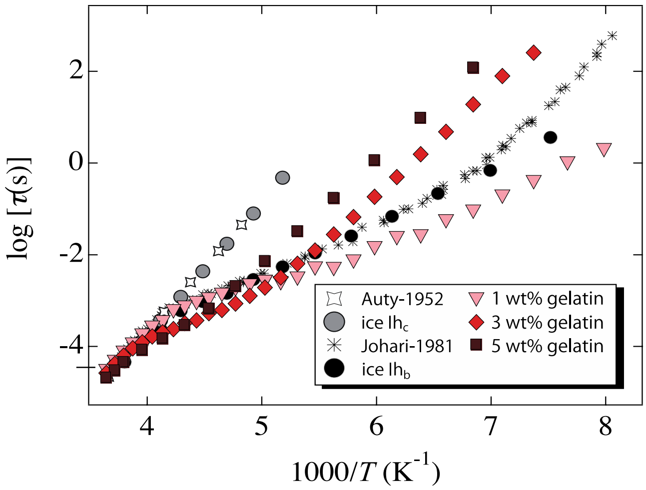

Figure. Temperature dependence of τ_{ice}. Triangles, diamonds and squares indicate 1, 3, 5 wt% gelatin-water mixtures respectively. Circles, open stars and stars are obtained by Sasaki et al.[3], Auty et al.[1] and Johari et al.[2] respectively.

Homopolyaminoacid Dynamics in Aqueous Solution

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ε-Polylysine (ε-PLL) is a homopolypeptide of aproximatelly 25–35 l-lysine residues with linkages between α-carboxyl groups and ε-amino groups. *ε*-PLL is a biodegradable polypeptide (water-soluble), edible and nontoxic toward humans and the environment, being suitable in a broad range of industrial applications such as food, medicine, environment and electronics (1). We are interested in the study of water dynamics in this polypeptide since water does not crystallizes on cooling even for high water contents and therefore it is suitable for studies at cryo-temperatures.

We have studied the dynamics of *ε*-PLL in solution at different water concentrations (from 30 to 45 wt% water content) and pH values (from 7 to 10) by means of dielectric spectroscopy in a broad frequency (10^{-2} – 50 GHz) and temperature range (140 – 300 K). The dielectric results of ε -PLL in aqueous solution show a rich dynamical behavior at low temperatures. Below T_g, three dynamical processes are resolved which can be related to the dynamics of amorphous water whereas above T_g, up to 5 dielectric relaxations were observed. This behavior is sensitive to variations in the pH of the solution.

In this work, we will analyze how the water and ε-PLL dynamics change with water content and pH.

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Novel Concept of Non-Debye Dipole for the Description of Dielectric Relaxation in glassy 2-Ethyl-1-Hexanol and Glycerol

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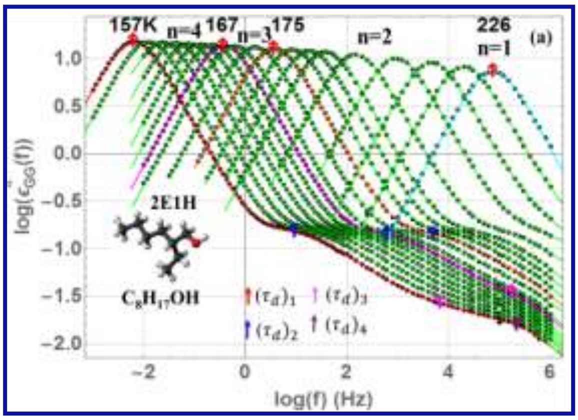
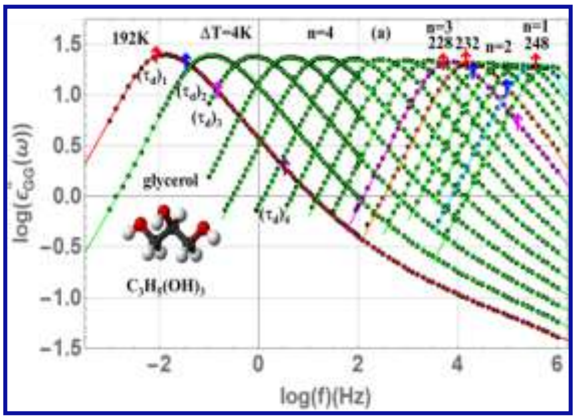
The physical ideas underlying in the dielectric spectra with results based on time-honored models of Cole-Cole, Davidson-Cole, Havriliak-Negami, Kohlrausch-Williams-Watts, Jonscher, Ngai and barrier hopping models are still debatable and do not offer satisfactory interpretation. Therefore, in the present work, a concept of intermolecule dipole-dipole interactions triggered non-Debye dipole, $(\mathbf{G})_n = ((1-g_d)\mathbf{G}_0)_n$, and dual dipoles $(\mathbf{G}_\pm)_n=(\mathbf{G}_0\pm\mathbf{G})_n$, $(\mathbf{G}_-)=g_d\mathbf{G}_0$ and $(\mathbf{G}_+)=(2-g_d)\mathbf{G}_0$ is introduced for the description of non-Debye relaxation, where $\mathbf{G}_0$ is a Debye dipole, and its magnitude is increased and decreased by a magnitude of $(1-g_d)(\mathbf{G}_0)$ and become $(\mathbf{G}_+)$ and $(\mathbf{G}_-)$, n is number of statistically highly independent process of subgroups of a molecule and they are discriminated by independent relaxation times $(\tau_d)_n$ of $(\mathbf{G}_0)_n$, $(\mathbf{G})_n$ and $(g_d)_n$, g_d is an exponent lies $0<g_d<1$, signifies interaction strength and connects time and frequency domains in the coupled form as t^{g_d} and ω^{g_d} for $(\mathbf{G}_-)$ dipole process, and t^{2-g_d} and ω^{2-g_d} for $(\mathbf{G}_+)$ dipole process, $g_d=1$ is for $\mathbf{G}_0$ dipole process During the molecular motion, instantaneous transfer of dipole moment $\mathbf{G}_0$ is not possible due to intermolecule dipole-dipole interaction and hence dipole $\mathbf{G}$ is created, where $\mathbf{G}_0$ is the N number dipole becoming N/2 pairs of $(\mathbf{G}_\pm)$. Dielectric and relaxation functions are derived for $(\mathbf{G}_\pm)$ dielectric dipole process (G. Govindaraj, AIP Conference Proceedings, 1731, 070025 (2016)). Typical resuts is shown in figures for supercooled 2-ethyl-1-hexanol and glycerol for the subgroups n=4,3,2,1 contributions depnding on temperature, where the black dots are data collected from the website http://glass.ruc.dk/data. The model delineate better physical insight, since the effect of many-body relaxation manifested in the dynamic properties has been incorporated fundamentally into proposed model in terms of $(\mathbf{G}_\pm)_n$. The α, β, γ and δ relaxations are desceibed in terms subgroup motion of a molceule, and model shows simple but profound physical picture for the non-Debye relaxation and shows excellent agreement with experimental observations.





Influence of hydratation and heat treaments on dielectric properties of wheathered granite.

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Nowadays, electromagnetic methods (figure 1a)) are communly used to assess properties in civil engeenering in order to replace destructive and nuclear methods[1,2]. However, dielectric behavior of investigated material needs to be understood to know how the EM waves interact with the material during investigations. Indeed low frequency methods such as capacitve methods show dispersion in results. Broadband dielectric spectroscopy turned out to be a powerful technique to figure out the dielectric behavior of rocks over a wide range of frequency and temperature. In the field, paved road is subjected to extreme conditions during manufacturing such as high and low temperature and sunny and wet weather. Heat treatments at 400°C and 1000°C were applied as well as hydratation and dehydratation state in order to confront the material to on-site conditions. Results highligth that water and microstructure have a huge impact on the complex peak observable at room temperature (figure 1b)) and that interfacial polarization migth be changed by these processes.

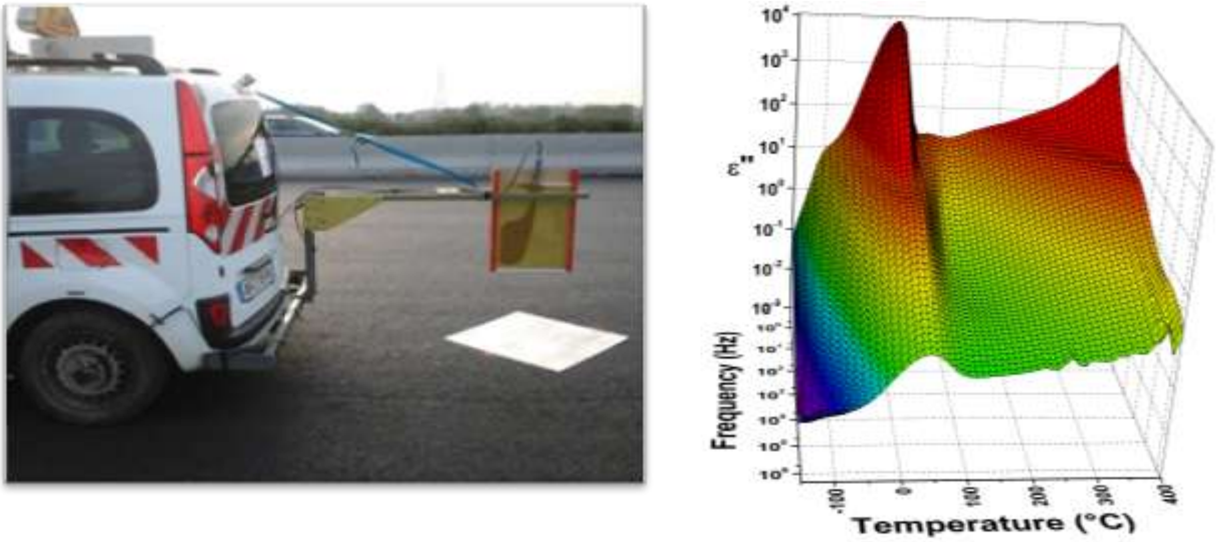

Figure 1: a) Step frequency radar b) Dielectric spectra of weathered granite from -150°C to 400°C and from 10^{-1} to 2.10^6 Hz without any treatment

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Space-time dynamics in water

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The intermediate position of liquids between gas and solid state naturally implies atoms and molecules of a liquid to participate simultaneously in the oscillatory and translational motions. The related physical model was offered by Frenkel [1] in the thirties of the last century and 30 years later was successfully used for interpretation of data of neutron scattering in liquid water. It was assumed that each molecule of water participates in Brownian like diffusion, being periodically localized to oscillate in a cage of its neighbors.

Here, analyzing the broadband conductivity spectrum of liquid water in the frequency range, 10^5 - 10^{14} Hz, we find its relaxation-resonance features to be indicators of Frenkel's translation-oscillation motion of charged particles. We develope a model of water structure whose dynamics is due to diffusion of particles, neutral H_2O molecules and H_3O^+ and OH^- ions. In accordance with the step shape of the conductivity spectrum the diffusing ions are assumed to be exposed to periodic localizations and mutual charge transformations. The mechanism of particle recharge is inter-oxygen proton hops happening during ion-molecular collisions. The particle delays modulate the diffusion rate while transformations modulate the diffusion visibility in the conductivity spectrum. Thus developing diffusion appears to be space-time structured.

The model links for the first time the dc conductivity, Debye and sub-Debye relaxations and the infrared absorption peak at 5.3 THz (180 cm^{-1}) consistently. We argue that the model is applicable to ice [2]. By the model the ambipolar space-time structured diffusion of H_3O^+ and OH^- ions is that molecular mechanizm responsible both in water and ice for the dc-conductivity, the dielectric constant and the Debye relaxation.

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Application of Broadband Dielectric Spectroscopy to Cultural Heritage: characterization and preservation of ancient paper artwork

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In this work we use broadband dielectric spectroscopy (BDS) to investigate the relaxation behaviour of water dipoles within the cellulose matrix of ancient paper artwork. Paper samples were taken from the unprinted guard sheets of ancient books –with printing date from XVI to XX century- from a private library (Fig.1, left panel). The BDS spectrum exhibits a well resolved peak that, due to its temperature and paper hydration dependence, can be attributed to water molecules inside the cellulose matrix pores. This peak shifts to higher frequencies in ancient paper (Fig. 1, right panel), likely due to the increased pore size caused by cellulose degradation following hydrolysis and/or oxidation. The relaxation times were shown to depend upon the book printing date and the age dependence suggested that the main degradation occurs within the first 100 years age of the book. Most interestingly, paper treatment with Halloysite nanotubes (HNT) restored the relaxation time characteristic of modern undegraded paper, suggesting that treatment with nanofillers may be effective in paper preservation.

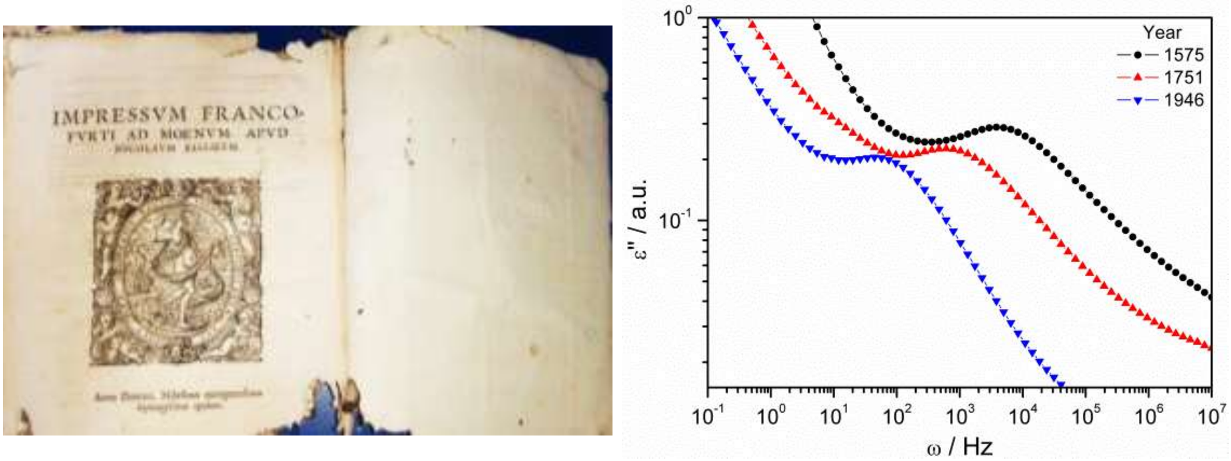

Figure 1. Left panel: XVI century book printed in Frankfurt, 1575. Right panel: Dielectric spectroscopy data on historical paper of different years.

Hydration shell dynamics driven by protein interface

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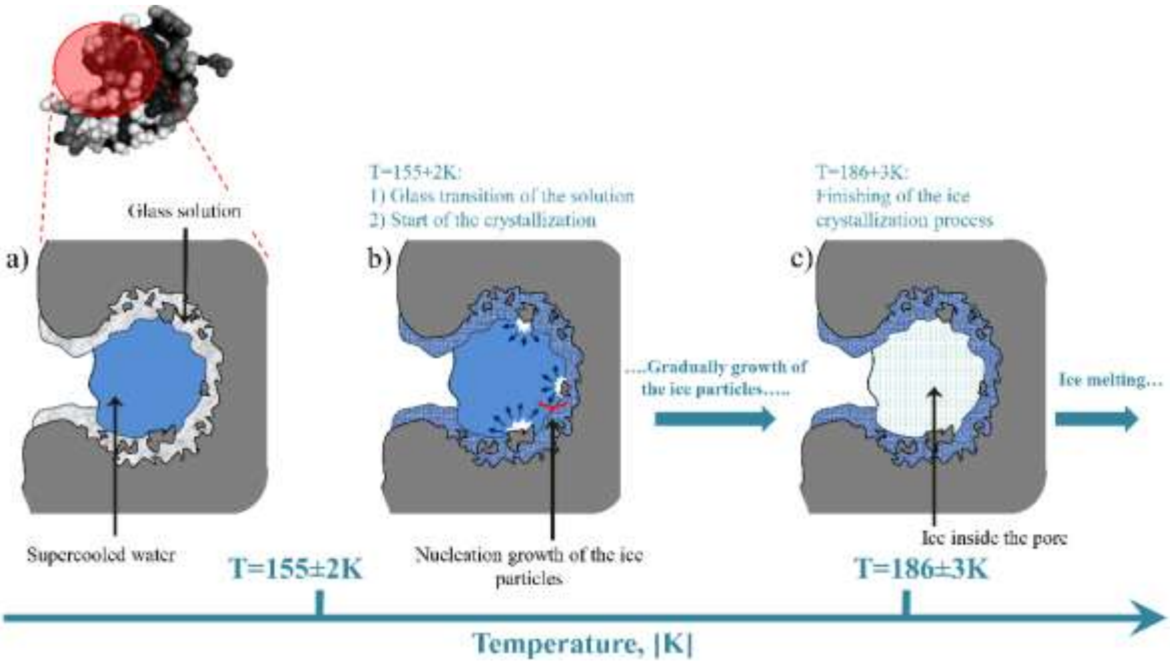
Water is of fundamental importance for life since it plays a critical role in biological systems. An organism can only function if its macromolecules and other bioactive molecules are hydrated. However, there is currently a gap in the understanding of how protein interfaces affect water's structure and properties. This work presents combined dielectric and calorimetric measurements of hydrated lysozyme powders with different levels of hydration in a broad temperature interval. We chose Lysozyme as a test sample since this globular protein has a well-defined pore with an active hydrophilic center inside. Based on the dielectric and calorimetric tests it was shown that a water quasi-solution, which contains the protein residues, has a glass transition at around 155±3K. The water confined in the pore of the active center of the lysozyme has its melting temperature at around 186±3K. Melting of confined water is believed to liberate the internal motions of protein macromolecules. A schematic presentation of the model, representing the two different water layers through the glass and the phase transitions is shown below. The full details of the research can be found in Ref.1



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Dielectric study of water in partially crystallized poly (ethylene glycol)-water mixtures

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The dielectric relaxation process of water was investigated for partially crystallized poly(vinyl pyrrolidone) (PVP), poly(ethylene imine) (PEI), poly(vinyl methyl ether) (PVME), poly(vinyl alcohol) (PVA)-water mixtures by dielectric spectroscopy[1]. On the other hand, the unique water structure around poly(ethylene glycol) (PEG) was studied by DSC[2]. According to the results, the two times melting of ice and eutectic of water–PEG were observed. By using dielectric spectroscopy, we observed relaxation process caused by molecular motion of water in the PEG–water mixtures to clarify the dynamics of water molecules at subzero temperatures under the two times melting.

According to the experimental results, the relaxation process originated mainly from reorientational motion of water was observed. A small potion of these process is contributed by local chain motion of PEG. Figure shows the temperature dependences of the relaxation sterength, $\Delta\varepsilon$, of water for PEG–water mixtures. The two times increases of $\Delta\varepsilon$ were observed for 10 – 40 wt.% PEG–water mixtures in a temperature range of −20 ºC – 0 ºC. On the other hand, the increase of $\Delta\varepsilon$ was observed only once for 50 wt.% PEG–water mixture at temperatures between −15 and −12 ºC. These results indicate that the melting of eutectic was observed for the all PEG–water mixtures at around −15 ºC. For the 10 – 40 wt.% PEG–water mixtures, the melting of ice were observed. 50 wt.% PEG–water mixture does not contain water enough to form ice crystal. The relaxation time of water for PEG–water mixtures are smaller than those of other polymer–water mixtures[1] below the melting temperature.

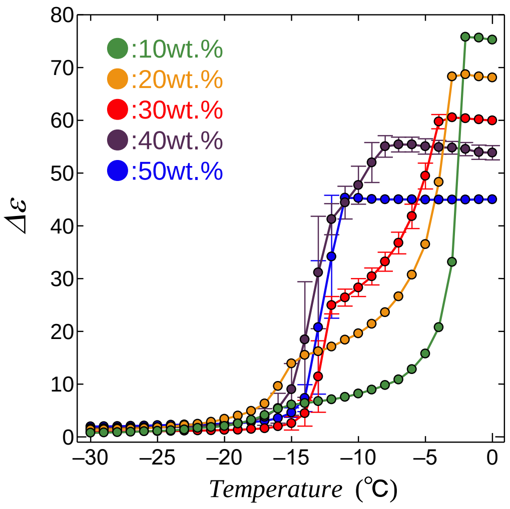

Figure. Temperature dependences of the relaxation strength of water for PEG–water mixtures with various PEG concentrations.

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Dynamic behaviors of aqueous solutions restricted with the volume phase transition of poly(acryl amide) gels

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Dynamics of solvent molecules restricted in the volume phase tansition of poly (acryl amide) gel with acetone-water mixtures have been studied in our former dielectric studies[1]. However, recent developments of dielectric studies on the hydrogen bonding network had not been reflected in those former studies. In the present work, we investigated molecular dynamics of solvent molecules in the volume phase transitio of poly (acryl amide) gels with three kinds of binary mixtures of water and organic solvents: dimethylsulfoxide (DMSO), acetone, and 1,4-dioxane. In addition, the self-diffusion coefficient, *D*, of protons included in water and solvent molecules were respectively obtained by Nuclear Magnetic Resonance measurements in order to compare with the dielectric relaxation time, τ, obtained by dielecric measurements. (Figures 1 and 2) Differences in *D* and τ values respectively obtained inside and outside gels suggest extents of the restriction on dynamic behaviors of solvent molecules. These results reflect differences in each volume phase transition and also the hydrogen bonding network. These behaviors should be also characterized well by fluctuations in *D* and τ values.

This work was partly supported by JSPS KAKENHI Grant Number 15K13554.

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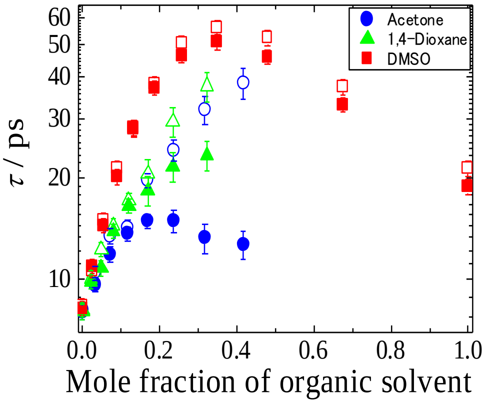

Figure 1. Composition dependences of the the relaxation time for various solvent mixtures in PAAm gels. Open and closed symbols indicate solvents inside and outside gels, respectively.

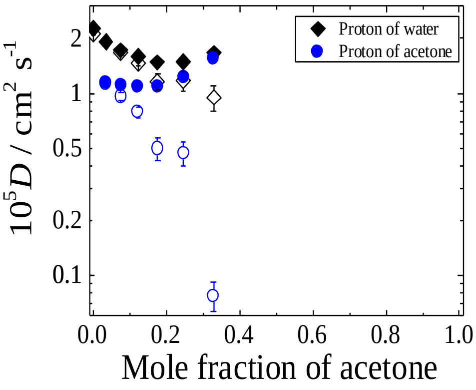

Figure 2. Composition dependences of the self-diffsion coefficient of water and aceton protons in PAAm gels. Open and closed symbols are same with those used in Figure 1.

Dielectric Study of the slow dynamics of proteins embedded in bioprotectant glassy matrices

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Sugars constitute a wide category of glass-forming systems that also perform a broad biological role in living matter. Besides functioning for energy storage, sugars show an outstanding ability in preserving structure and functionality of biomolecules, which has been largely exploited in food, pharmaceutical, and biotechnology sciences to optimize protein lyophilization and long-term storage of pharmaceuticals [1]. Indeed, the largely employed lyophilization process alone imposes remarkable stresses on proteins and peptides, which can subsequently lead to detrimental conformational changes [2,3]. Inclusion in the protein formulation of non-specific stabilizers such as sugars, is therefore vital for minimizing the perturbation of protein native structure during lyophilization [4]. The nanoscopic mechanisms through which sugar matrices act as stabilizers are still unclear, although their glassy nature [5] and the hydrogen-bond mediated interaction with the protein [6] seem to be decisive. Reasonably, both phenomena are expected to affect the protein dynamics. A detailed investigation of the role of specific interactions between the protein groups and the sugars is still needed.

In the present work we have studied lysozyme embedded in different bioprotectant matrices, such as sugars and polyols. The systems were obtained from freeze-drying procedure. Indeed, bioprotectant glassy matrices have shown to induce a noticeable retardation of protein molecular movements and an increase of both glass transition and denaturation temperatures. Moreover, through a careful dielectric spectroscopy study it has been possible to find how the specific interactions between protein and sugars affect the secondary relaxations of the systems.

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Electrical properties of lithium ferrite / poly(lactic acid) composites

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Lithium ferrite, $LiFe_5O_8$ (LFO), is attractive for several technological applications due to its electrical and magnetic properties. This material is known to be dependent on the preparation route and starting materials. In this work $LiFe_5O_8$ powders were synthetised by wet ball-milling method and using lithium and iron nitrates as raw materials and then heat treated at 1100 ^oC, which is the temperature where LFO phase is the main crystal phase. The aim of this work is to evaluate the electrical properties of the LFO powders embedded in a polymer matrix. Several composites were prepared by dispersing the LFO with concentrations ranging from 0 to 20% (wt/wt) in the biopolymer poly(lactic acid).

The obtained composites, were studied by XRD, TGA, DSC and broadband dielctric spectroscopy (BDS). The BDS measurements were performed in the frequency range between 10^{-1} Hz and 10^6 Hz and in function of temperature ($-100 \leq T \leq 140$ ^oC).

The electrical properties were related with the structure and with the concentration of LFO particles in the amorphous matrix.

In the samples with lower LFO concentration (≤ 5% wt/wt) the BDS results are characterized by the detection of two relaxations: a dominant α process, associated with the dynamical glass transition; and a secondary process. Both are influenced by conductivity. The α relaxation process becomes broader as the concentration of LFO particles increases. The samples with higher LFO content (≥ 7.5%) the dielectric properties are dominated by the conductivity.

Different mixture laws were used to analyse the conductivity in function of LFO particles concentration.

The temperature dependence of the detected relaxation processes and conductivity was analysed, allowing the construction of a relaxation map, which provides the dynamic fingerprint of the material.

Complex dynamics of a fluorinated vinylidene cyanide copolymer highlighted by dielectric relaxation spectroscopy

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The complex dynamics of a nearly alternating copolymer of vinylidene cyanide (1,1-dicyanoethylene, VCN) with 2,2,2-trifluoroethyl methacrylate (TFEMA), including two α- relaxations with diverging time scale in the glass transition temperature range, was thoroughly characterized by dielectric spectroscopy over wide temperature and frequency ranges and analyzed in the frame of the Ngai's Coupling Model. The dielectric relaxation strength as well as the glass transition temperature, the temperature dependence of the α-relaxation time and the corresponding distribution of relaxation times were all larger than those of a reference TFEMA homopolymer, as expected from the introduction of the stiffening VCN units all along the macromolecular chain. The effect of casting solvent and applied poling electric field on the copolymer dielectric strength suggests the onset of local orientational order involving the strong dipoles in the VCN units, a requirement for piezo-and pyroelectricity in amorphous polymers.

KEYWORDS
2,2,2-trifluoroethyl methacrylate; vinylidene cyanide; dielectric spectroscopy; amorphous copolymer; coupling model; piezoelectricity.

ACKNOWLEDGMENT
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Thermoresponsive behavior of PNIPAM- and PMDEGA-based copolymers: comparative investigation

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Thermoresponsive copolymers have attracted considerable scientific interest due to their unique properties and their potential applications [1]. These materials respond strongly to a small change of temperature. This behavior is due to a balance between attractive monomer–water interactions and monomer-monomer interactions.

In the present work we investigate the thermoresponsive transition and the organization of water in two different thermoresponsive copolymers. The first one is the well-known poly (N-*iso*-propyl acrylamide) (PNIPAM). Its phase transitions are accompanied by the formation of inter- and/or intrachain hydrogen bond above their LCSTs [2]. The second one contains poly(methoxy diethylenglycol acrylate) (PMDEGA), which undergoes a phase transition through thermally induced dehydration but without formation of the inter- and/or intrachain hydrogen bond in the polymer-rich phase [3]. Both the thermoresponsive blocks are tethered to polystyrene (PS) blocks, which form the hydrophobic core of the micelles above the critical micelle concetration (CMC) [4].

In the present work we employ Small-Angle Neutron Scattering (SANS), Differential Scanning Calorimetry (DSC) and broadband Dielectric Relaxation Spectroscopy (DRS) techniques for our investigation. Most importantly, Dielectric Spectroscopy, which has been widely used in the investigation of the hydration properties of materials [5] and also for the investigation of the thermoresponsive behavior of polymers [6], aims, both, at the study of the thermoresponsive behavior and the re-organisation of water in the system during the transition.

The combined studies gives us results on the kinetics of the transition and long-range morphology as a function of temperature and are discussed in terms of micelles structure, clustering of micelles and water organization during the demixing/remixing process in the two classes of thermoresponsive copolymers.

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Dielectric and calorimetric studies on poly(lauryl acrylate)-b-poly(N-isopropyl acrylamide) block copolymers

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One of the most studied thermoresponsive polymers is poly(N-isopropylacrylamide) (PNIPAM), which presents a lower critical solution temperature (LCST) at around 32^{o}C in aqueous media [1]. Great variety of thermoresponsive block copolymers comprising hydrophilic PNIPAM blocks and short hydrophobic blocks have been synthesized and studied in solutions and in bulk. In the present work we study the poly(lauryl acrylate)-b-poly(N-isopropyl acrylamide) block copolymer (PLA-b-PNIPAM) with a weight ratio 30/70. The copolymer is synthesized by RAFT polymerization by sequential addition of monomers, starting with the synthesis of the PLA block. Our aim here is to study the effects of PLA confinement, within the glassy matrix of PNIPAM, on the dynamics of PLA chains and how these effects are influenced by water absorption.

We employ Differential Scanning Calorimetry (DSC) and broadband Dielectric Spectroscopy (BDS) techniques in order to study comparatively the thermal transitions and molecular dynamics of PLA homopolymer and PLA confined in the copolymer. We study both, dry samples and hydrated samples (at water contents variying from 0 to about 50% w/w).

Our measurements on PLA homopolymer reveal crystallization/melting events and a weak glass transition. BDS, in addition, provides evidence for the activation of the polyethylene like segmental relaxation of the side chains in the homopolymer [2]. These effects are present also in the copolymer, although with reduced intensity, indicating the occurrence of phase separation. It is interesting that our results show that PLA chains plasticize the PNIMAM phase (at least in the dry state). Contrary to PLA homopolymer, PLA-b-PNIPAM copolymer absorbs quite large amounts of water when is exposed to enviroments with varied relative humidities, as expected due to hydrophilic PNIPAM component. Our measurements allow to study the organization of water within the phase separated copolymer and its impact on the dynamics of both, the hydrophobic PLA and the hydrophilic PNIPAM segments.

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Broadband Dielectric Spectrocopy on H_2O, D_2O, and $H_2{}^{18}O$, and Theoretical Calculations on the THz Spectral Component

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Feng Zhang[2], Kaoru Ohta[2], Hideaki Shirota[3], Shinji Saito[4],
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It is well known that liquid water interacts with electromagnetic waves over a broad frequency range. For example, the collective rotational relaxation has its dielectric spectra from MHz to GHz frequency region, and the spectral component in the THz region is suggested to be due to fluctuation of the hydrogen bonding network. These spectral components in the different frequency regions overlab with each other. Therefore, it is necessary to perform dielectric spectroscopic measuremets in a broad frequency region. In this study, we chose H_2O, $H_2{}^{18}O$, and D_2O as samples. We also measure the dielectric spectra by changing temperature from 273 K to 353 K. In the microwave region (200 MHz~20 GHz), the complex dielectric constants were measured by a vector network analyzer. In the sub-THz region (40 GHz~300 GHz) and THz region (300 GHz~2.5 THz), a pair of spiral and dipole type photoconductive antenna were used for generation and detection of the electromagnetic waves, respectively [1]. In the higher frequency side of the THz region (2.5 THz~7 THz), the THz pulse was generated by focusing the output and its second harmonics from a regenerative amplifier into air. For the far-IR and mid-IR regions, the absorption spectra were measured by using FTIR spectrometers. Figure 1 shows the complex dielectric spectra of water at 20 C from 200 MHz to 30 THz. the results fo the specrtal analysis using the following function are shown.

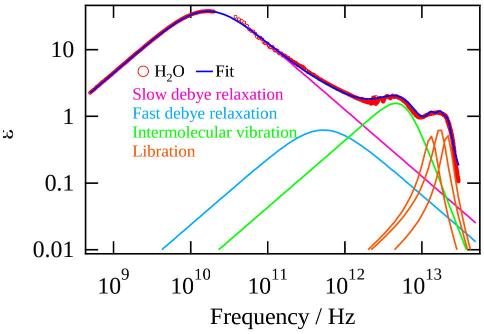

Figure 1. Complex dielectric spectra of H_2O at 20 C from 200 MHz to 30 THz.

$$\tilde{\varepsilon}(\nu) = \frac{\Delta\varepsilon_1}{1 - i2\pi\nu\tau_1} + \frac{\Delta\varepsilon_2}{1 - i2\pi\nu\tau_2} + \frac{A_3}{\nu_3^2 - \nu^2 - i\nu\gamma_3} + \sum_{i=4}^{6} \frac{A_i}{\nu_i^2 - \nu^2 - i\nu\gamma_i} + \varepsilon_\infty$$

The Raman spectra provide complementary information about the molecular dyanmics in liquids. We also discuss the low-frequency Raman spectra of water obtained by optical Kerr effect measurements with femtosecond laser pulse. We also perfomed molecular dynamics simulation and instateneous normal mode analysis for liquid water to understand the spectral component in the THz frequency region.

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THz properties of BST bulk and film samples

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Such ferroelectric materials as barium strontium titanate (BST) are very attractive for microwave applications. The rapid development of communications systems requires development of advanced materials for millimeter and submillimeter waves [1, 2] and BST shows interesting features for high frequency applications. For this work, BST targets were prepared by solid-state reaction and films with thickness of about 2 microns were grown on intrinsic silicon and (100) MgO single crystal substrates by using Pulsed Laser Deposition. Morphological and structural investigations were carried out on BST ceramics and films. THz time-domain measurements were performed on BST films by using the transmission setup, which provides the highest incident power, hence the best signal to noise ratio. On one side, in the case of Si substrates, the measurement bandwidth was limited to 7 THz, which is the maximum bandwidth of the spectrometer. On the other side, the MgO substrates limited to about 4 THz the measurements for BST films deposited on such substrates. The dielectric parameters of the BST films were obtained by substracting the substrate response. Acknowledgement: This work was partially supported by a grant of the Ministry of National Education, CNCS – UEFISCDI, project number PN-II-ID-PCE-2012-4-0654.

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Microwave dielectric characterization up to 1200 °C

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The dielectric characterization over wide temperature intervals can have a twofold relevance: it can elucidate fundamental aspects of the investigated samples, as the origin of the main dielectric contributions or the occurrence of phase transitions; moreover, it can provide information necessary for applicative purposes, as in the case of electromagnetic assisted material processing.

In the framework of the project HELM [1], a setup for the dielectric characterization at ca. 2.45 GHz has been developed, which enables measurements from room T to 1200 °C. The setup is based on a cylindrical microwave cavity operating on TM_{0n0} modes and on a shuttle system, the latter enabling a fast displacement of the sample from the furnace to the cavity and back, following the basic structure described in Ref.[2]. The sample can be characterized in less than 300 ms since its displacement from the furnace. In the design of the setup and in the definition of the data acquisition procedure, a particular attention has been dedicated to the accuracy of the measurements. Different solutions have been implemented to limit the distortion of the microwave curves, to remove at each T the measurement bias due to the sample holder, to control and minimize the sample temperature inhomogeneity. Finally, much efforts have been dedicated to the development of a methodology enabling a rigorous determination of the dielectric quantities from the electromagnetic data, in a very wide range of conditions covering insulating as well as conducting materials. As a result, it is possible to characterize samples experiencing a very large variation in the dielectric properties with the temperature, including phase transitions from insulating to conducting states, in a single measurement session.

Some illustrative results will be shown, obtained with SiC and Si samples. In particular, the Si exhibits impressive variations in the dielectric properties from room temperture to 1200 °C. In particular, both the ε' and the ε'' of silicon show a monotonic increase with T of about 7-fold and 270-fold, respectively.

Finally, the extension above 1500 °C of the maximum measurement temperature of the setup is possible with simple modifications and has already been scheduled.

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Terahertz dielectric properties of Mg- and Zn-based silicate ceramics

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Mg_2SiO_4 (MSO) and Zn_2SiO_4 (ZSO) ceramics have been suggested as very good candidates for millimeter wave (MMW) applications [1]. Their potential for development of MMW devices was extrapolated using a direct proportionality between microwave (MW) dielectric loss and frequency. However, due to the lattice defects induced during processing, the extrinsic losses can considerably increase the total MW dielectric loss [2] and, therefore, the extrapolation to higher frequency can lead to inaccurate outcome. On the other hand, the estimation of the intrinsic dielectric loss in MW and MMW domain by using submillimeter wave and infrared spectroscopic techniques [3, 4] yields to better results. In this work, we report on the terahertz dielectric properties of the MSO and ZSO ceramics. Morphological and structural characterizations of the samples were performed using scanning electron microscopy and X-ray diffraction. The dielectric properties were investigated in the 0.2 - 4 THz range by using the Aispec IRS 200 PRO terahertz time-domain spectrometer on transmission set-up. The data have been extracted from time-domain results by using a commercial software (TeraLyzer). The dielectric loss of MSO samples increases monotonically with the increasing of the frequency. On the other hand, a strong absorption peak was evidenced at 2.3 THz for ZSO samples. Experimental data will be discussed and compared with those obtained in MW for MSO and ZSO dielectric resonators.

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Intrinsic and extrinsic contributions in (Ba,Sr)TiO_3 ferroelectric ceramics studied by broad-band dielectric spectroscopy

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Ferroelectric materials, bulk and thin films, have been intensively investigated for a large variety of applications [1]. Among these, polycrystalline ones are the most utilized as they offer cost-effective solutions for devices. However, compared to the single-crystals, the dielectric response of the ferroelectric ceramics is strongly influenced by its microstructure (porosity, grain sizes, interfaces, defects, etc.) Therefore, the temperature-dependent dielectric spectroscopy can be used to distinguish between intrinsic and extrinsic contributions in polycrystalline materials. (Ba,Sr)TiO_3 ferroelectric solid solutions are very attractive for microwave tunable components due to their permittivity variation with an applied electric field [2]. Paraelectric compositions with Curie point close to room temperature exhibit low dielectric loss [3] and univocal dependence on electric field of the permittivity. On this line, $Ba_{0.6}Sr_{0.4}TiO_3$ samples prepared by conventional ceramic technology were structurally and morphologically characterized by X-ray diffraction and scanning electron microscopy [4]. The broad-band frequency behavior (10 mHz to 10 MHz) of the dielectric function were carried out by using Alpha Analyzer from Novocontrol in a range from -110 ^oC to 200 ^oC. Some relaxation processes were revealed in both ferroelectric and paraelectric phases. These processes were analyzed using the Havriliak-Negami formalism. In addition to intrinsic contributions, the conductive processes occurs at temperatures higher than 100 ^oC, which follow an Arrhenius law with an activation energies of about 0.8 eV. Experimental data will be discussed and compared with some others (Ba,Sr)TiO_3 compositions.

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Centrosymmetric tetragonal B-site doped calcium copper titanate and its dielectric tunability

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Calcium copper titanate on doping Te^{4+} at Ti^{4+} sites transformed structurally to centrosymmetric tetragonal double perovskite. Indeed selected area electron diffraction studies carried out on Te doped ceramics corroborate the refined X-ray diffraction data. The dielectric tunability obtained as a function of applied DC field in Te doped calcium copper titanate ceramics was superior to that of undoped samples. Te doping at the B-site of double perovskite shows a huge influence in the dielectric behavior of calcium copper titanate ceramics in temperature range of 30-750 K. Raman studies done on these ceramics with temperature variation also show similar behavior.

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Dielectric relaxation in textured ferroelectric vinylidene fluoride copolymers with different morphology

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Broadband dielectric spectroscopy was used to study low-temperature molecular mobility in two ferroelectric vinylidene fluoride (VDF) - tetrafluoroethylene (TFE) copolymer films textured via uniaxial drawing. Initial isotropic films were prepared by crystallization from acetone (#1) and dimethylformamide (#2) solutions. SAXS measurements showed that supramolecular structures of the initial films are different: there are lamellar crystals that are packed in stacks which form micron-sized spherulites in film #2, while there are no stacks and spherulites in the film #1. These differences caused different morphologies after uniaxial drawing: the film #1 is optically transparent, while a strong opalescence is observed in the film #2. This means that there are a lot of microcracks in the volume of film #2. It is confirmed indirectly by lower values of dielectric permittivity in the film #2.

This paper is devoted to the study of the role of the morphology in dielectric relaxation both above (α_a-relaxation) and below (β-relaxation) the glass transition temperature T_g.

It was found that for the microporous film #2 T_g is a little higher (227 K) than in the film #1 (222 K). At the same time more significant changes were found for the fragility parameter *m* [1], which describes the deviation of the temperature dependence of the segmental relaxation time from the Arrhenius behavior. *m* was found to be 95 for the film #1 and 111 for the film #2. Transition into the glassy state for the film #2 is not accompanied by collapse of the micropores, since the values of the dielectric permittivity below T_g are lower than in the film #1.

Activation parameters of the relaxation processes for the films #1 and #2 differ significantly, especially for the local mobility (β-relaxation): for example, the activation entropy is two times higher for the film #2. This result is in qualitative agreement with the data reported in [2], where it was found that the fragility parameter and the activation entropy are sensitive to the details of the relaxation process.

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Electric and magnetic properties of Fe_2O_3--SiO_2--PbO glass manufacturing by traditional melt-quenching method and twin rollers fast-cooling method.

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Glasses of the composition x Fe_2O_3--50 SiO_2--(50-x) PbO (x=12.5, 15 and 17.5) exhibit interesting magnetic properties [1]. Samples of sillicate-iron-lead oxide glasses were prepared by two different methods: a traditional melt quenching and fast-cooling technique. Electrical and magnetic properties were measured. Micrography of the samples was obtained by SEM microscopy. Magnetic properties of samples obtained by a traditional melt-quenching method and glasses obtained by the twin rollers method have been compared. The electrical properties were investigated by impedance spectroscopy□. The magnetic properties were measured with Physical Properties Measurement System (PPMS).

The impedance spectroscopy research of samples which was made by twin rollers fast-cooling method showed that glasses have low activation energy (about 0.5 eV) of direct current conduction. Frequency dependence of conduction was analyzed on the basis of Elliot's paper [2] and an electrical conduction mechanism was proposed.

Magnetic measurements of glasses with a composition x Fe_2O_3--50 SiO_2--(50-x) PbO showed that glasses have narrow magnetic hysteresis loops. The glasses produced by twin rollers fast cooling method have the magnetic hysteresis loop narrower than glasses these produced by a traditional melt quenching method, while increase in the amount of Fe_2O_3 increases coersivity.

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Interplay between the long range static ordering and dynamical heterogeneities determining the dynamics of the plastic crystal and ordinary liquid phases of the same material

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Broadband Dielectric spectroscopy and X ray diffraction has been applied to investigate molecular dynamics as well as structural properties of levoglucosan. It turned out that this compound similarly as ethanol is able to form internal ordering characteristic for the Orientationally Disordered Crystal [ODIC], called usually plastic crystal, as well as supercooled liquid after hyperquenching it from the melt to the nitrogen temperatures. Hence it is a perfect candidate to probe the relationship between internal structure and molecular dynamics. We obtained that there is long range correlations up to 30 nm between molecules in the superccoled and Orientationally Disordered Crystal as found from X ray diffractions measurements. Interestingly the dynamics of the structural process in levoglucosan prepared in both states seems to be almost the same. Structural relaxation times in the superccoled phase are slightly faster with respect to the ones determined in ODIC state. Moreover, it was shown that distribution of the relaxation times is slightly broader in the supercooled liquid. That might indicate more heterogeneous dynamics which is related to the higher degree of freedom in this state. In addition we also calculated number of dynamically correlated molecules N_C using Berthier approach for levoglucosan in ODIC and superccoled phases. It was found that $N_c \approx 115$ molecules at the glass transition temperature in both cases. This result stays in contrast to the current discussion indicating that number of dynamically correlated molecules is expected to be lower in plastic crystal phase. What is more Nc does not change to much with lowering temperature in such systems. However it is worth to mention that in the literature different systems of various intermolecular interactions as well as structures are compared. On the other hand herein results obtained for the same molecules characterized by various degree of ordering are discussed. The collected data might be very useful in better understanding of the relationship between structure and dynamical properties of the investigated glass formers.

Reorientational Dynamics in 1-F-adamantane

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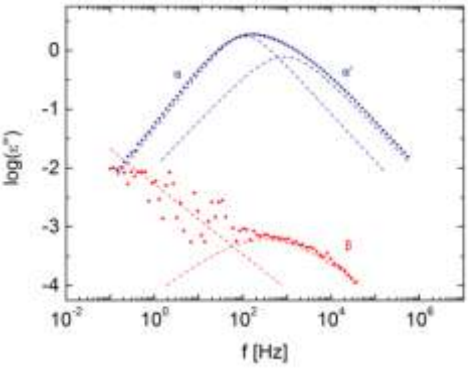
The physics of disordered materials is particularly intriguing. In particular, a full understanding of the origin of the glass transition phenomenon in orientationally disordered systems is still lacking. Among materials with orientational disorder, adamantane derivatives are found to display a rich polymorphism that has stimulated a large number of experimental and theoretical investigations aimed at understanding the molecular dynamics in the high-temperature phases and, to less extent, that of low-temperature phases.[1-4]

The polymorphism of 1-Fluoro-adamantane has been studied by X-ray powder diffraction and broadband dielectric spectroscopy. This small, rigid molecule forms a "well-ordered" tetragonal structure in which disorder is limited to the statistical site occupancy of the fluorine atom (shared among four possible equivalent sites). Such a "simple" disorder gives rise to rather rich relaxation dynamic including a "bimodal" primary relaxation (α) associated with the time average fluctuations of the molecular dipole around the three- and two-fold molecular (C_{3v} symmetry) axes and crystal axes (space group $P\bar{4}2_1c$), and a secondary (β) Johari-Goldstein relaxation.



Our work demonstrates the existence of two distinct primary relaxations for separate rotational degrees of freedom of the same rigid molecule. Our findings imply that orientationally disordered phases display richer and more varied relaxation dynamics than conventional glass formers which is, probably due to the softness and anisotropy of the intermolecular interactions in these translationally ordered solids.

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Volume phase transition in thermo-responsive hydrogels as seen by dynamical mechanical analysis, dielectric spectroscopy and complementary techniques

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Currently, thermo-responsive, biocompatible hydrogels are regarded as promising drug delivery systems. They exhibit volume phase transition (VPT) – abrupt change in volume leading to significant changes in their physico-chemical properties [1]. The latest investigations show that the VPT temperature strongly depends on the content of bioactive substances including ibuprofen sodium salt [2]. Moreover Raman spectroscopy studied suggests that observed effect relates probably to changes in polymer hydration, not to specific polymer-drug interactions. Thus the studies on dynamic properties of thermo-responsive hydrogels are especially important, as the dynamic of VPT depends mainly on dynamics of polymer chains constituting the gel network and diffusive properties of liquid medium fulfilled it.

In this work dynamical mechanical analysis, dielectric spectroscopy and complementary techniques (differential scanning calorimetry, vibrational spectroscopy and fluorescence correlation spectroscopy) were used to study volume phase transitions in two thermo-responsive hydrogel systems:

- polyvinylmethylether (PVME) hydrogels obtained by electron beam irradiation (EBI) of water solution of linear PVME, as a model system (PVME has one the simplest structure among other thermo-sensitive polymers),
- poly(2-(2-methoxyethoxy)ethyl methacrylate) (PMEO$_2$MA) hydrogels obtained by both EBI method as well as by atom transfer radical polymerisation (ATRP).

The complementarity of the results obtained with use of different techniques will be discussed.

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The authors would like to acknowledge dr Y. A. Yoon and prof. K. Matyjaszewski (Department of Chemistry, Carnegie Mellon University, Pittsburgh, USA) for synthesis of PMEO$_2$MA gels. Investigations were partially supported by Polish National Science Center in frame of grant No 2013/09/B/ST4/03010.

Molecular dynamics of S-ibuprofen sodium salt in solid, solution and hydrogel states.

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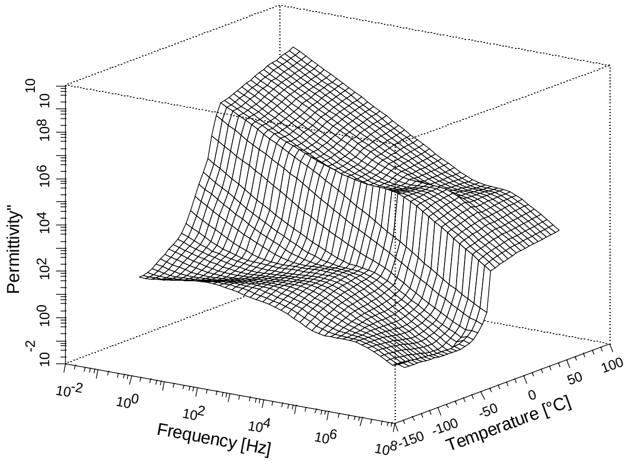
(S)-2-(4-(2-Methylpropyl)phenyl)propanoic acid (S-ibuprofen) is one the most popular nonsteroidal anti-inflammatory drugs. It is used to treat fever, mild to moderate pain, painful menstruation, osteoarthritis, dental pain, headaches, and pain from kidney stones. It is used also for inflammatory diseases and for pericarditis and patent ductus arteriosus.

Ibuprofen exhibits high tendency for crystallization and limited solubility in water, thus, for medical purposes, the sodium salt of ibuprofen is usually used. It may be used as a component of pills, syrups or injection fluids. It is important to notice that the form of a drug is a crucial point taking into account drug activity. In a case of painkillers and anti-inflammatory medicines the fast reaction is especially required.

There are only some papers reveal the relaxation process of ibuprofen in solid phase. It is interesting to compare relaxation processes of ibuprofen in other states useful for medical treatment such as solutions and gels. Moreover, our last investigations showed high influence of ibuprofen sodium salt on volume phase transition in thermo-responsive hydrogels of poly(2-(2-methoxyethoxy)ethyl dimethacrylate) [1].



In this work the molecular dynamics of S-ibuprofen sodium salt (more bio-active enantiomer) in solid state, in aqueous solutions with different concentration as well as in thermo-responsive hydrogels based on polyvinylmethylether will be discussed. In the aqueous systems two regions can be observed: below and above 0°C. The relaxation process seen above 0°C shifts to higher frequency region with increasing concentration of S-ibuprofen sodium salt. Three relaxations seen below 0°C seems to be nonsensitive on salt concetration.

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The authors would like to acknowledge dr S. Kadlubowski (Institute of Applied Radiation Chemistry, Lodz University of Technology, Lodz, Poland) for synthesis of gel samples. Investigations were partially supported by Polish National Science Center in frame of grant No 2013/09/B/ST4/03010.

The implication of various molecular interactions on dielectric behavior of cimetidine base and cimetidine hydrochloride

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We employed broadband dielectric spectroscopy to characterize the molecular dynamics of two related materials, cimetidine base and cimetidine hydrochloride, with similar structural skeleton but different character of molecular interactions involved (ionic vs. non-ionic sample). BDS experiments performed at ambient and elevated pressures, combined with rheology and temperature modulated calorimetry studies, revealed a significant discrepancies in supercooled dynamics of both samples. The strong character of electrostatic interactions results in slower dynamics of ionic counterpart, manifested by higher Tg value. On the other hand, some similarities were found in the glassy dynamics. The dielectric response of cimetidine hydrochloride reveals parallel features to those observed previously for other molten hydrochloride salts, among them decoupling between the timescales of structural and ionic displacements, affirming universal character of behavior presented herein.

The effect of temperature and pressure changes on the crystallization kinetics of fenofibrate

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Fenofibrate is a BCS class II lipid modifying agent used in the treatment of cardiovascular diseases. Except the pharmaceutical activity, is it a modeled glass-forming system to study crystallization. In this contribution, we have performed a detailed investigation on the crystallization tendency of the amorphous fenofibrate at ambient and elevated pressure. For that, a numerous of the experimental techniques were employed. This has included dielectric spectroscopy, optical microscopy, x-ray diffraction and differential scanning calorimetry. Based on results collected at atmospheric pressure we have determined the temperature dependances of the crystal growth and overall crystallization rates. Moreover, we have demonstrated that recrystallization of fenofibrate from the supercooled liquid state produces a crystalline material which is a mixture of the two polymorphs (the most thermodynamically stable form I and metastable form II). The crystallization kinetics studies carried out along isochronal conditions indicate for slowing down the crystallization progress with increasing pressure. The effect of the path dependance on the crystallization rate has been considered as well. Finally, we will also show that high-pressure crystallization of fenofibrate enables to avoid metastable polymorph II in the recrystallized material.

Effect of Polymer Molecular Weight and Concentration on Crystallization Behavior of Indomethacin-PVP Amorphous Solid Dispersions: Role of drug-polymer interaction and viscosity in controlling global mobility

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Use of amorphous solid dispersions (ASDs) can be an effective strategy to increase the oral bioavailability of poorly water soluble drugs. The amorphous state of the drug confers a higher apparent solubility than its crystalline cournterpart. However, the potential for the drug to crystallize in the ASD may severely limits its usefulness. The objectives of this work are to: i) study the effect of polymer molecular weight and concentration on the drug-polymer interactions in ASDs, ii) investigate the role of molecular mobility in the crystallization behavior of ASDs and, iii) develop a basis for rational polymer selection.

Indomethacin (IMC) was chosen as the model drug. Polyvinylpyrrolidone (PVP) with different molecular weights (grades K12, K17 and K30) was the model polymer because of its biocompatibility and ability to interact with IMC via hydrogen bonding. ASDs with different polymer concentrations (up to 30% w/w) were prepared by solvent evaporation followed by melt quenching. Over a wide temperature range in the supercooled region, the α-relaxation times were obtained using dielectric spectroscopy, which provided a measure of molecular mobility. In the same temperature interval, IMC crystallization was studied isothermally, at several temperatures.

Increase in polymer concentration in the ASDs led to a reduction in the molecular mobility of the system, attributed to increase in the extent of drug-polymer interactions. Isothermal crystallization studies revealed a corresponding longer lag time and a decrease in the magnitude of the crystallization rate constant. For a fixed polymer concentration, higher molecular weight polymers are found to be more effective in reducing the mobility and in slowing down IMC crystallization (Figs. 1 and 2).

An increase in the polymer molecular weight will render the matrix more viscous – an effect expected to become pronouned at high polymer concentrations. Also, with an increase in molecular weight, the elongated chain length will make the polymer more flexible in nature and may affect the extent of drug-polymer interactions.Currently, solid state NMR is being used to determine the extent of interaction between drug and polymer in ASDs. These experiments will reveal the influence of polymer molecular weight on the drug-polymer interactions. Our final goal is to determine the influence of viscosity and the extent of drug-polymer interaction on both molecular mobility and drug crystallization kinetics. An understanding of the relative importance of drug-polymer inteaction and viscosity can potentially provide a tool for rational selection of the polymer and its grade.

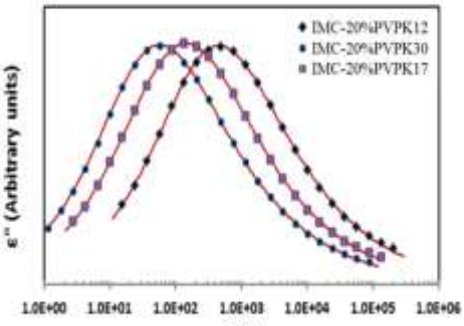

Fig. 1: Frequency dependence of ε″ for PVP-IMC ASDs with different molecular weights of PVP (at 80 ^{0}C).

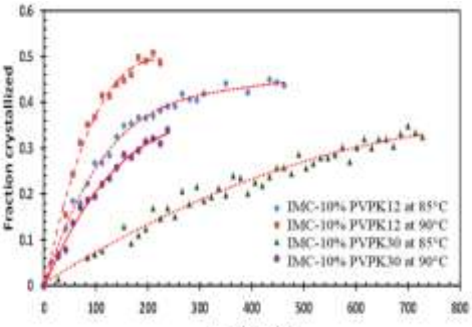

Fig. 2: Effect of polymer molecular weight on the IMC crystallization in ASDs.

Absence of correlation of fragility with dynamics and thermodynamics properties in binary mixtures of glass-formers

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Fragility, considered by many as a key parameter of the dynamics of glassforming liquids, has been the centre of attention of many studies of glass transition. Many attempts were made to correlate fragility with other properties and quantities of neat glassformers. The non-exponentiality parameter (1-β_K) is the most closely associated with the structural α- relaxation, and its correlation with fragility index *m* or lack of it seems more relevant [1,2,3,4]

In this study we examine the relation of fragility to (1-β_K) as well as the coupling parameter *n* in the family of mixtures of either one of two polar rigid molecules tert-butylpyridine and Quinaldine with tristyrene at different concentrations. Even in these closely related systems where the difference is only the concentration of the same component in the mixture, we find neither correlation of the fragility index *m* with (1-β_K), nor *m* with $T_{g.}$ In the mixtures of Quinaldine with tristyrene, we found no correlation between *m* and ΔC_p. Most dramatic are the findings of *anticorrelation* between *m* and *n* and *anticorrelation* between *m* and T_g instead of correlations.

The difference in packing the rigid polar molecules as compared with the more flexible and non-polar tristyrene molecules suggests lesser influence of volume and entropy on fragility as the tri-styrene content in the mixture is increased. The results, particularly the anticorrelation between *m* and *n*, support the proposal that the temperature dependence of τ_α and fragility are governed not only by the thermodynamic quantities including volume and entropy but also the cooperative many-molecule relaxation dynamics (reflected by the *n* parameter)[5].

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Electro-Rheological Effects in Glass-Forming Liquids: Does Entropy Control the Relaxation Time?

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The objectives of this study were to: i) investigate the dielectric relaxation behavior of viscous liquids in the nonlinear response regime via application of high dc electric fields, ii) assess the field induced changes in entropy and of their impacts on the relaxation times, and iii) discuss the observed electro-rheological effects on the basis of the Adam-Gibbs model.

Dielectric relaxation spectra of eight glass-forming systems varying in their fragility values have been measured close to their glass transition temperatures (T_g) in the presence of dc-bias fields ranging from 100 to 500 kV/cm. For each sample, two distinct field induced effects are observed: a reduction of the relaxation amplitude and an increase in the primary structural relaxation time While the amplitude change is typical of the well-known normal dielectric saturation, the field induced increase in viscosity is recognized as a new source of nonlinear dielectric behavior. These non-linear effects are found to scale with E^2, and the magnitude of the electro-rheological effect varies within a factor of 12 for the compounds of this study when compared at the same magnitude of the applied field. The field induced relative change in relaxation time is correlated with the extent of reduction in thermodynamic entropy that originates from applying the high field at constant temperature, see Fig. 1. On the basis of the Adam-Gibbs model, these experimental results facilitate a comparison of temperature versus field induced changes in entropy and of their impacts on the dielectric relaxation times.

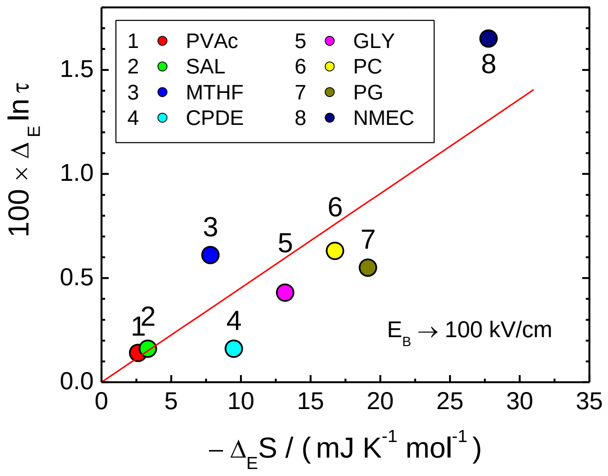

Fig. 1 Compilation of the field induced relative change of the relaxation time, $\Delta_E \ln \tau$, versus the field induced entropy change, $\Delta_E S$, for all eight compounds of this study. The values of $\Delta_E \ln \tau$ are rescaled by the field squared to reflect the magnitude expected for a field of E_B = 100 kV/cm.

High pressure dielectric studies on the plastic crystal, 1,6-anhydro-D-glucose and strongly H-bonded liquid, D-glucose

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Molecular dynamics of plastic crystal (1,6-anhydro-D-glucose) and strongly H-bonded system (D-glucose) was investigated at high pressures. We found that there are many similarities between both compounds i.e. *i*) structural dynamics is weakly sensitive to pressure in D-glucose and levoglucosan (it is well reflected in the low pressure coefficient of the glass transition and orientational glass transition temperatures: $\partial T_g / \partial p$ and $\partial T_g{}^{o} / \partial p$= 60 K/GPa for D-glucose and 1,6-anhydro-D-glucose, respectively) *ii*) the shape of the primary relaxation stays constant independently on the thermodynamic conditions *iii*) isobaric fragility drops with compression (this change is much more significant in the case of D-glucose with respect to levoglucosan, where the fragility changes only slightly with pressure). However, there are also some significant discrepancies in the activation volume which seem to be very significant at short relaxation times and tend to disappear in the close vicinity of the glass transition temperature. This aspect is closely related to the mechanism of molecular movements of 1,6-anhydro-D-glucose and D-glucose molecules. Interestingly, it was also demonstrated, that $\partial T_g{}^{o} / \partial p$ evaluated for 1,6-anhydro-D-glucose is enormously high with respect to other plastic crystals studied so far.. Interestingly, the same situation is observed in the case of the isobaric fragility which is the highest among all materials forming ODIC phase. Such behavior is due to formation of three dimensional H-bonded network. In addition, the relationship between dc conductivity and structural relaxation at high pressure in plastic crystal was tested. It turned out, that at higher compression decoupling between both variables becomes more significant. Finally, we carried out investigations on the ODIC–crystal phase transition (lewoglucosan) at isochronal conditions. It was shown that as the system becomes more compressed, formation of more ordered state is favored. This result mimics the impact of pressure on the crystallization of fully disordered supercooled van der Walls liquids.

Pressure dependence of Johari-Goldstein β-relaxation in 1-methylindole

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The Johari-Goldstein relaxation is a process observed in many glass-formers of various kind[1,2] and its behaviour, with respect to the primitive α relaxation, can be predicted by the Coupling Model[2].

Its cooperative nature is reflected by its pressure and density dependence[3] and can be used as a smoking gun to distinguish it from other types of relaxation[4].

Recently, Xiangqian Li, Li-Min Wang and coworkers, have found evidence of a secondary process in glassy 1-methylindole[5], a small, planar, polar and rigid molecule. However, this fast process is inconsistent with the Coupling Model and is probably due to in-plane rotational motion. The dynamics of other similar molecules have been compared to that of 1-methylindole and the presence of a slower, Johari- Goldstein type of relaxation was predicted.

We studied the glassy state of the molecule by applying elevated pressure in isothermal and isobaric dielectric measurements. The results give a deeper insight of the processes involved in the dynamics of the glassy state.

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Modeling of the dielectric and relaxation properties of nanostructured metal-containing films

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The study discusses the correlation of the empirical parameters of the well-known Havrilyak-Negami formula with the physical characteristics of metal-nanostructuted composites. The approach utilized is based on the non-phenomenological theory of complex permittivity of the material [1-3]. The absolute values and temperature dependence of the empirical parameters are found to be dependent on the nanoparticle parameters and the energy of electrons in the traps created around the metal nanoparticles. In addition, while the frequency dependence of the dielectric permittivity in the region of the maxima is well described by the empirical formula, the temperature dependence on the other hand is much harder to interpret, and the empirical parameters are not readily ascribed any physical meaning.

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Extracting material net properties of monomolecular coverages from BDS measurements with nano-structured electrode arrangements

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Recently, Broadband Dielectric Spectroscopy (BDS) has been combined with a nano-structured electrode arrangement to investigate glassy dynamics in monomolecular layers [1] and even isolated polymer chains [2]. Thereby, strongly insulating silica nano-structures serve as spacers between highly conductive silicon electrodes enabling electrode-to-electrode distances of only ~40 nm. Since this is still considerably larger than the height of the actual sample material, a major fraction of the capacitor volume is empty. Consequently, the measured signal is an average of several contributions, including the dielectric properties of the sample itself, the spacer material and the gap between the electrodes. Due to the particular geometry of the components in-between the electrodes, the composition of their contributions is not straight-forward. To unravel the individual dielectric functions of all components an equivalent circuit model, which considers their arrangement, is employed. Using BDS spectra of poly(2-vinylpyridine) (P2VP) polymer brushes and condensed isolated P2VP polymer chains as examples it is demonstrated how to unravel molecular relaxations, polarization effects and charge transport as well as the extraction of the net properties of these processes.

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Study of the dielectric properties of nanofluids using impedance spectroscopy

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Nanofluids are suspensions of nanoparticles in a fluidic medium, which can be water, ethylene-glycol, oil, etc. Among different nanoparticles, carbon nanotubes detain exceptional physical properties, being the best-suited nanoparticle to be added to be base fluid. The thermal properties of such carbon-based nanofluids have been extensively studied, but the electrical properties are not quite understood and well stablished. In this research work, it was prepared nanofluids with different volume fractions of carbon nanotubes. The base fluids are a mixture of ethylene-glycol and stilled water. In order to guarantee a high-quality dispersion of the carbon nanotubes into the base fluid, it was performed a chemical treatment on the nanoparticles surface, followed by ultrasonication mixing to ensure a proper colloidal stability.

Impedance spectroscopy measurements were performed on the nanofluids, in the frequency range from 100 Hz to 1 MHz, and temperatures between 300 and 370 K. A single relaxation time, described by the equation of Debye, cannot be used to explain the observed dielectric relaxation. We have analysed the data using the Cole-Cole model, which adjusts correctly the data. The calculated relaxation parameters were correlated with the filler concentration.

Using compatibilization to tune dielectric properties resulting from conductivity mediated polarization at polymer-polymer, polymer-particle and polymer with particle-electrode interfaces in stacked polymer films and polymer blends

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The properties of PαMSAN/PMMA interfaces were tailored in stacked polymer films and biphasic polymer blends with an interfacially localized random copolymer (PS-r-PMMA). Conductivity contrast of the constituents resulted in interfacial entrapment of the PαMSAN charges at the PMMA/copolymer interface, whose relaxation strength scales with the ratio of the structure dimension of PαMSAN to the Debye length (L_D). With increasing copolymer concentration, a pronounced decrease in L_D in comparison to the reduction of the characteristic length scale of the PαMSAN domains resulted in an increase of the interfacial capacitance (Fig. 1).[1] For biphasic blends with MWNTs, the MWNTs selectively localize in PαMSAN, resulting in entrapment of MWNTs charges at the PαMSAN interface. Its dielectric strength was tuned by the copolymer with an improved connectivity and refinement of PαMSAN laden with MWNTs, achieved by varying the copolymer concentration (Fig. 1), molecular weight and architecture (block or random). From the microcapacitor behavior and dielectric mixing models it could be derived that the interfacial capacitance was governed by the connectivity of the capacitors of PαMSAN between adjacent MWNTs, as the intrinsic length scale was unaffected. Finally, the compatibilizer also affects the polymer-electrode polarization as the improved percolation enhances the amount of charge carriers able to reach the interface.

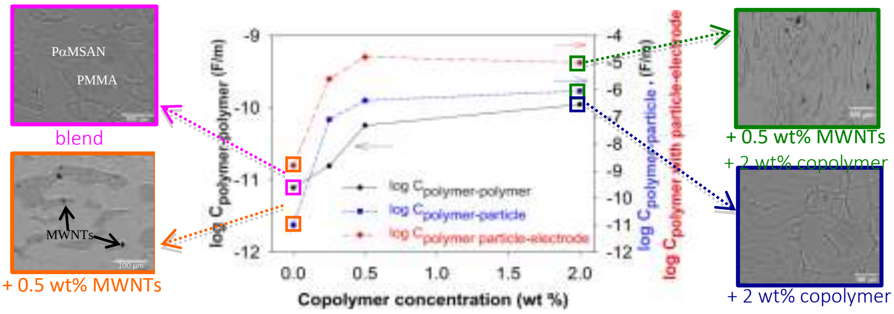

Fig. 1: Dependence of interfacial capacitance on copolymer concentration at PαMSAN-PMMA/copolymer, PαMSAN–MWNTs, PαMSAN with MWNTs-electrode interfaces. Representative optical micrographs are shown.

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Study of the interfacial polarisation in SiO_2/ Si bi-layer strucrure by dielectric spectroscopy

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SiO_2/Si bi-layer structure was studied by means of Broadband Dielectric Spectroscopy (BDS) in the frequency range 0,1 Hz-1 MHz and a temperature interval from 10 to 150° C. At sufficient high temperatures, electrical conductivity effects give rise to high values of ε' and ε'' increasing with decreasing frequency. The slopes of $\varepsilon''(f)$ determined on the frequency interval 0,1-1 Hz are varying from 0.61 to 0.79 and increasing with temperature, proving the existence of a conduction phenomenon which tends towards the dc conductivity effect when increasing temperature. Two relaxation processes or interfacial polarizations known as the Maxwell-Wagner-Sillars (MWS) effect are identified: the first in the frequency domain 0,1-100 Hz and temperatures above 70° C is allotted to the near interface consists of a few atomic layers containing Si atoms in intermediate oxidation states; the second in the frequency domain between 100 Hz-1 MHz for temperatures varying from 0 to 150° C attributed to the second region or interface which extends about 30 A° into the SiO_2 over layer. These two effects obey to the Arrhenius law with corresponding activation energy E_a of 0,408 and 0,163 eV respectively.

Dielectric and conductivity studies of Polypyridinium triflate with carbon nanotubes

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Electrochromic polymers are currently attracting interest in science and industry due to their fundamental spectroelectrochemical properties and possible commercial applications. Application of conjugated polymers in organic electron devices, such as smart windows or displays, is limited by their switching times between bleached and colored states. Switching ability of a polymer material is determined by the ion and electron transport in the polymer layer. One of the methods to overcome the limitations is based on the addition of carbon nanotubes (CNTs).

Polypyridinium salts (PV) is a well-known class of electrochromic polyelectrolytes. Unique electrical and mechanical properties of carbon nanotubes (CNTs) as well as the ability to interact with PV due to the presence of conjugated carbon rings make them promising candidates for modification of electrochromic properties of PV.

Electrochromic nanocomposites were prepared by non-covalent functionalization of CNTs by PV. Nanocomposite films were prepared by the spin-coating method.

It was found that the addition of carbon nanotubes alters the morphology of polymer film and measured response times indicate that composite films switch faster between redox states than pristine PV [1].

Unique dielectric properties were observed at low frequencies in nanocomposite films: below ~10Hz the magnitude of ε' decreases rapidly and its sign switches abruptly from positive to negative at a characteristic frequency. This frequency increases when a dc-bias (both positive and negative) is applied to the film. Similar behavior was previously reported in [2] for nanoparticle materials.

The conductivity of polymer films with the addition of CNTs was significantly improved.

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DSC, Optical and dielectric properties of polyvinyl alcohol/ cellulose nanocomposites

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Film formation, processability and hydrophilicity of polyhydroxy polymers such as poly (vinyl alcohol) (PVA) make them some of the most commonly used polymers in industry. They are also noted for their biocompatibility and biodegradability. So and as a water-soluble polymer, PVA has been widely used as a matrix for the preparation of nanocomposites. In fact, the hydroxyl groups on partially hydrolyzed PVA are expected to interact with the hydrophilic surfaces of the cellulose nanofibers, leading to strong hydrogen bonding. It was reported that composites reinforced with cellulose nanofibers have only shown moderate mechanical performance.

In this study, cellulose nanofibers (NFC) derived from *eucalyptus pulp* were utilized as reinforcement for polyvinyl alcohol. So, nanocomposites with different concentrations of cellulose nanofiber (3, 5, 7, 10 and 13% by weight) were prepared and their properties were compared with neat PVA. Thermal (Differential scanning calorimeter), Optical (FTIR) and dielectric spectroscopy of all compositions were evaluated.

Thermal analysis demonstrated that the presence of NFC did not have a large effect on glass transition temperature, while it sensibly modified the melting temperature of the PVA matrix, as well as the crystallization temperature, due to the nucleating action of the nanofillers. An analysis of the NFC content effect on the conductive properties of the nanocomposites was also carried out. The dielectric spectra exhibit conductivity phenomena at low frequencies and high temperatures: dipolar, Maxwell-Wagner- Sillars (MWS) and electrode polarization (EP) conductive processes were observed in the nanocomposite samples.

Dielectric Properties measurements in large frequency and temperature ranges of natural rubber-cellulose nanocomposites

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Natural rubber (NR) isolated from Hevea Brasiliens and reinforced with different amounts of cellulose nanowhiskers (extracted from the rachis of date palm tree) was investigated using differential scanning calorimetry and dielectric spectroscopy in the frequency range 0.1Hz to 1MHz, and the temperature range -80 to 200°C. The experimental dielectric data were analyzed within the formalisms of dielectric permittivity, complex conductivity and complex impedance. The results were discussed in terms of dc conductivity, MWS polarization and electrode polarization. Emphasis is put on the investigation of electrical conductivity andconductivity effects. The results revealed that the mixtures of polysaccharide nanocrystals and latex led to the production of nanocomposite materials with drastically enhanced dielectric properties, especially at $T>Tg$ of the matrix, by virtue of the formation of a whiskers network, even when the whiskers volume fraction was only a few percent. The formation of this rigid network, resulting from strong interactions between whiskers, was assumed to be governed by a percolation mechanism and exhibit better physical and chemical properties then their bulk counterparts.

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Structure and Dynamics of 2,3,6,7,10,11-hexakis[hexyloxy] triphenylene (HAT6) in Nanoporous Anodic Aluminum Oxide Membranes

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Due to their chemical structure, a rigid disk-like aromatic core and flexible alkyl chains attached to the core, discotic liquid crystals (DLCs) can organize and stack themselves into columns in a hexagonal columnar mesophase, a mesophase in between the plastic crystalline and isotropic phase. The overlap of the π-orbitals of the aromatic core in the hexagonal columnar mesophase leads to a high charge-carrier mobility along the column axis – these columns can be considered as “moleculer nanowires”- making liquid crystals a promising class of materials for electronic applications. Previous studies on DLCs showed that the phase behavior of DLCs is susceptible to nano-confinement [1,2]. Here in this study, the thermotropic collective orientational order of 2,3,6,7,10,11-hexakis[hexyloxy] triphenylene (HAT6), a triphenylene-based DLC, and the effects of nano-confinment on of its phase behavior were investigated by broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC). HAT6 was embedded into nanoporous anodic aluminum oxide membranes by melt infiltration in the isotropic phase under argon atmosphere. The filled membranes have the thickness of 80 µm and the diameter of 15 mm and parallel aligned tubular nanopores having the pore diameters of 25, 40, 80 and 180 nm. The filling degree for each sample was checked by thermogravimetric analysis (TGA) in order to ensure complete filling. The bulk HAT6 forms, a hexagonal columnar phase between the isotropic phase above 371 K, and the plastic crystalline phase below 340 K. Unlike the bulk, the confined HAT6 forms two peaks in the heat flow during the plastic crystalline-to-hexagonal columnar phase transition, which might be the evidence of two different phase structures close to the wall and in the pore center. Moreover, the isotropic-to-columnar transition of the confined HAT6 shifts with decreasing pore diameter to lower temperatures.

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Dielectric investigations on carbon nanomembranes

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Carbon nanomembranes (CNMs) are synthetic 2D carbon sheets prepared from aromatic self-assembled monolayers (SAMs). Their physical and chemical properties depend strongly on their structure and molecular composition, which can be tailored by using various precursor molecules. Multilayer carbon nanomembrances (CNMs) could pave the way for a new type of ultrathin dielectrics or functional coatings with tunable electrical, optical, and chemical properties. Due to their molecular thickness, they can also be regarded as “interfaces without bulk” separating regions for membrane applications.

To understand the electron induced chemical transformation of the aromatic SAM, broadband dielectric spectroscopy (BDS) was utilized to characterize the dielectric properties of CNMs. To this end, *p*-terphenylthiol (TPT) was used as a precursor molecule to prepare model CNMs with a thickness of approximately 1.5 nm, and multilayer stacks consisting of 5, 10, 15 and 20 TPT–CNMs were fabricated by adopting a simple poly(methyl methacrylate)-based tranfer method. For all the multilayer CNM stacks, we observed a clear relaxation process which shifs to higher frequencies with increasing temperature. The temperature dependence of the relaxation rate of this process is independent of film thickness and can be well described by a common VFT function, indicating a corporative motion. This relaxation process could be attributed to intrinisic dipoles in CNMs as the crosslinking of adjacent dehydrogenated carbon centers can be sterically hindered. This finding will also give an insight into the mass transfer mechanisms through CNMs such as intrinsic pores in the CNMs. The origin of the relaxation process was further discussed with a detailed anaylsis of the dielectric strength. This is the first BDS measurment on TPT–CNMs.

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Effect of the fluid flow on the distribution of carbon nanotubes during the injection moulding of polymer nanocomposites

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Polymer nanocomposites (PNCs) are candidates to exploit the excellent electrical, thermal and mechanical properties of nanomaterials like carbon nanotubes (CNTs) or graphene. To take full advantage of their properties, CNTs must be well dispersed in the polymeric matrix and preserve their original aspect ratio, which is not easy due to the high tendency of CNTs to form agglomerates. However, the relationship between processing parameters, the nanostructure achieved and the resulting properties of PNCs is not yet fully understood.

Broadband dielectric spectroscopy (BDS) is a promising volumetric technique to characterise CNT distribution in PNCs in industrial environments, as it can be used in a fast and non-destructive way, unlike high-resolution characterisation techniques such as atomic force microscopy or electron microscopy.

In this work, we consider how the electrical properties of CNT nanocomposites are affected by the fluid flow during the mould filling process in injection moulding.

Moulds with two-gate and one-gate configurations are used to produce specimens with and without weld lines, respectively, in order to study the differences in CNT alignment and distribution. BDS is applied at different regions along standard tensile bars, where significant differences in flow can be observed in mould filling simulations, to study the spatial variation of the local electrical properties.

The conductivity in the direction of the thickness of the sample was observed to increase in the weld line region, suggesting an increase in the amount of CNTs perpendicular to the surface. Different PNCs with varying CNT concentrations will be considered and the degree of polymer crystallinity will be analysed.

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Molecular Dynamics of PMPS in uniaxial Pores of varying nanometric Diameter (5-10 nm)

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Broadband Dielectric Spectroscopy (BDS) is employed to study the effects of a 2D–confinement on the rotational diffusion of polymethylphenylsiloxane (PMPS), a classical glass-forming polymer. To prepare uniaxial nanopores (diameter of 5 nm, 7 nm, 10 nm) pure silica wafers are etched with hydrofluoric acid and oxidized at ~ 900°C. After this treatment PMPS is incorporated by capillary suction. The molecular dynamics of the confined PMPS splits at a temperature T_{split} into two relaxation processes having both Vogel–Fulcher–Tammann temperature dependences. One coincides with the bulk–like dynamics, while the second is significantly faster. The latter is assigned to fluctuations of polymer segments close to the pore walls. The splitting temperature T_{split} increases with decreasing pore diameter. This confinement effect is explained based on the inherent length scale of the dynamic glass transition, which increases with decreasing temperature until its growth is limited by the external constraints.

Effect of architecture on polymer crystallization and dynamics under AAO confinement

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Polymer exists under nanoscale confinement in a range of applications including nanoporous membranes for gas separation, flow through nanopores as rheology modifiers in fracking fluids, and in nanoscale lithography for semiconductor manufacturing. In such applications, polymer conformation and dynamics at the segmental and chain length scales is of importance. Anodic aluminum oxide (AAO) is an ideal template in investigating the 2D confinement due to the uniform, cylindrical structure of nanopores. Recent studies of linear polymer (e.g. iPP[1], PEO[2,3]) in AAO confinement show that by confining polymers to small isolated AAO nanopores, a transformation from heterogeneous nucleation to homogeneous nucleation is observed. Dielectric spectroscopy results from the former work[3] revealed first a broadening of relaxation peak of linear PEO inside AAO and second a speed up of dynamics in smaller pore size.

In this work, we employ two star PEOs and study the effect of end groups and of molecular weight on the polymer crystallization both in the bulk and under confinement. Concerning the expected slowing down of long-range dynamics by the star-shaped structure, we investigate the segmental dynamics by dielectric spectroscopy. In the confinement, long-range dynamics pertinent to star relaxation are affecting the homogeneous nucleation temperature. The homogeneous nucleation temperatures for the star polymers agree with that of linear ones provided that the arm molecular weight is used instead of the total molecular weight. On the other hand, the segmental dynamics speed-up on confinement.

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Dielectric investigations of attograms and zeptograms of matter

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Dielectric investigations on attograms and zeptograms of matter (1 attograms = 1e – 18 gram, 1 zeptogram = 1e – 21 gram) offer the possibility of exploring the transition between nanoscience and physics of molecules, opening the door for fundamental questions in soft-matter physics, such as for instance "What is the minimum amount of matter necessary to "define" the material properties?". Based on the concept of employing nanocontainers as measurement cells, an experimental development allowing one to crystallize extremely small amounts of matter (attograms and zeptograms) under high electric fields (i.e. 1e6 V/cm) is demonstrated in the present contribution. Evidence is brought for the ability of manipulating the state of matter.

Electrical and dielectric properties of composite materials: the role of morphology, volume fraction, form factor, orientation and presence of interphases

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A general route to adjust the electrical performance of polymeric materials represents the composite approach, when fillers of different morphologies, sizes and electrical properties are embedded into a polymer matrix. The resulting macroscopic properties of the composite material depend on the volume fraction and the spatial distribution of the fillers as well as on their interaction with the polymeric material. The current contribution aims to develop a complete theoretical description of the electrical and dielectric properties of multiphase composite materials in systematic dependence on morphology, volume fraction, form factor, orientation, volume distribution of the fillers and interphases. Three scientific challenges are addressed: (a) Understanding the impact of internal interfaces and interphases on the dielectric response of composite materials; (b) Detailed quantitative analysis of the impact of heterogeneity on the spectral dependence of existing molecular relaxation processes; (c) To develop and propose a criterion which enables one to distinguish, in the case heterogeneous materials, true relaxation processes from dielectric dispersions caused by the phenomenon of interfacial polarization.

Evidence of proton wires in biomolecules by dielectric spectroscopy

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The study of the interactions between biomolecules and water are of fundamental importance. An example of these interactions is the proton transfer, which is a mechanism carried out by the organized motion of water molecules. In this work we have measured the dielectric properties of some amino acid solutions at low frequencies (100 Hz-1 MHz). Our results show a strong experimental evidence of a proton wire mechanism in L-glutamic acid. This process is noticed as an extension of the low frequency wing which induces a small relaxation time associated to the ionic dynamics. A similar dielectric behavior was observed for ovalbumin. Because L-glutamic acid is an important constituent in this protein, we believe that its dielectric response is driven by processes produced by such amino acid. Our findings may lead to a further understanding of water-biomolecules interactions, which guide the main functions of a cell. For instance, the synaptic transmission between neuronal cells is mediated by glutamate receptors, and the precise position of the water molecule involved in such communication is decisive.

Dielectric Spectroscopy of Biological Materials

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Charge transport within proteins is crucial for existence of living organisms. However, the microscopic mechanisms of short- and long-range charge transfer within them is still an open issue. We report on the study of the conductivity mechanisms and molecular dynamics in lyophilized *Shewanella oneidensis* MR-1 extracellular matrix and filaments (SOEMF) that is carried out using the technical and theoretical spectroscopic arsenal developed within the solid state physical community and that was never used in its full strength for the studies of charge dynamics in bio-systems. The spectra of SOEMF, together with those of the reference materials, cytochrome C and bovine serum albumin, were measured at frequencies from 1 Hz to 10^{12} Hz and at temperatures from 10 K to 300 K. We find intriguing similarities between the response of these biological objects and the wide variety of disordered and amorphous inorganic materials. The spectra of SOEMF and cytochrome C demonstrate universal dielectric response (UDR) of the Jonscher type and the well-known scaling relations for the dynamical conductivity and dielectric permittivity. The low-temperature spectra of SOEMF and cytochrome C, and the spectra of bovine serum albumin at all temperatures, reveal the existence of the so-called second dielectric universality, the nearly constant loss (NCL) behavior. In addition, the disorder driven boson peak phenomenon manifests itself in the temperature behavior of the specific heat of the three materials, in the form of a bump below 10 K. Modeling with the Lorentzian the boson peak density of states allows to estimate the Debye temperatures of the studied compounds. We believe that our observations in quite different biological specimens of the dynamical temperature-frequency behaviors that are universal for inorganic disordered systems indicate the generality of these universalities for the entire class of biological materials and opens up new opportunities for their spectroscopic studies.

Mixed ion-polaron transport in ZnO-WO_3-P_2O_5 glasses containing Na_2O and Li_2O

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Oxide glasses containing mobile alkali ions and transition metal oxides (TMO) such as WO_3, Fe_2O_3, V_2O_5, MoO_3 exhibit mixed ion-polaron conductivity. While ionic conductivity depends on the concentration and mobility of alkali ions, polaronic transport follows the small polaron hopping mechanism and it is mainly controlled by the overall amount of TMO and fraction of TM ions in different valence states.

The aim of this study was to investigate the mechanism of electrical transport in glasses containing WO_3 and Na^+/Li^+ ions, namely, glasses from series $x$$WO_3$-(30-0.5x)$Na_2O$-(30-0.5x)ZnO-40$P_2O_5$, $0 \leq x \leq 60$ (mol%) and $x$$WO_3$-(30-0.5x)$Li_2O$-(30-0.5x)ZnO-40$P_2O_5$, $0 \leq x \leq 40$ (mol%). Electrical properties of glasses were measured by impedance spectroscopy in the wide frequency and temperature range (0.01 Hz - 2 MHz, 303 - 513 K). The fraction of tungsten ions in different valence states, W^{5+}/W_{tot}, was determined from the temperature dependence of magnetization, measured with SQUID magnetometer, and analysed using the Curie constant attributed to the isolated paramagnetic centres W^{5+}.

Electrical conductivity of $x$$WO_3$-(30-0.5x)$Na_2O$-(30-0.5x)ZnO-40$P_2O_5$ glasses is almost constant up to x=30 mol%, whereas for glasses with higher WO_3 content conductivity increases drastically due to an increase in polaronic contribution. On the other hand, glasses from $x$$WO_3$-(30-0.5x)$Li_2O$-(30-0.5x)ZnO-40$P_2O_5$ series exhibit minimum in conductivity at approximately x=20 mol%. This phenomenon can be related to the coupling of ionic and polaronic transport which decreases effective mobility of both types of charge carriers. Comparing glasses between the two series, in the compositional region where the ionic conductivity prevails (up to x=30 mol% WO_3), glasses containing Na^+ show higher conductivities than glasses with Li^+ despite the smaller size of the later ion. This result suggests that lithium ions have lower mobility in these glasses due to a strong interactions with the structural units in the glass network. The reverse trend for glasses with 40 mol% of WO_3 is attributed entirely to the polaronic transport since glass containing Li_2O has higher fraction of W^{5+} ions (W^{5+}/W_{tot}=1.3%) than the glass containig Na_2O (W^{5+}/W_{tot}=0.8%).

Enhanced photoluminescence and dielectric permittivity in Cr doped ZnS nanoparticles

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Recently, semiconductor nanostructures have been intensely studied due to their remarkable properties at nanoscale levels. The fact that their properties can be tuned by adding some dopants, make them attractive for various applications such as dielectrics, photovoltaic, nanoelectronics, photo-electronics and sensing devices. ZnS, an important II-VI semiconductor has band gap ≈ 3.7 eV in bulk form and can change upto ≈ 4.1 eV in nanoparticles. Further increase upto 4.8 eV in the bandgap has been reported when ZnS nanoparticles are doped with suitable amount of Pb or Fe [1-3]. The larger bandgap of dopant nanoparticles is advantageous for dielectric applications.

Here, we will report the influence of Cr doping on the structural, optical and dielectric properties of the ZnS nanoparticles. Specifically we will shoe that Cr doped ZnS nanoparticles show simultaneous enhancement in optical as well as dielectric properties ($\boldsymbol{\varepsilon}' \approx 10^6$). At the end, we will discuss the possible reasons for the enhancement in these physical properties of Cr doped ZnS nanoparticles. applications.

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Study of conduction mechanisms and dielectric properties of ZnO/MgO solid composites

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In this paper, (1-x)ZnO/xMgO solid composites, where x= 10 and 20 %, were prepared at high temperature 1200°C by a solid–state method. The microstructure, dielectric relaxation characteristics and the electrical properties were investigated via scanning electron microscopy (SEM) and NOVOCONTROL dielectric system in wide frequency 0.1Hz–1MHz and temperature range -100–100°C, respectively. Results showed that the grain size was decreased with increasing MgO content. For the dielectric properties, a strong dispersion of permittivity constants was observed at low frequency, which can be attributed to interfacial relaxation (MWS). For the electrical properties, the frequency dependence of ac conductivity is interpreted in terms of Jonscher's law. The ac electrical conduction in ZnO/MgO composites is analysed by different processes, which can be attributed to several models, the hopping correlated barrier (CBH) and the overlapping large polaron tunnelling model for both composites 0.9ZnO/0.1MgO and 0.8ZnO/0.2MgO.

Keywords: ZnMgO composite, Dielectric relaxation, Electrical properties, Overlapping large polaron tunnel (OLPT).

New insight into ion transport through the dynamic modulus studies

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Over the last couple of decades the importance of the ionic liquids (ILs) in the industrial processes continue to rise. The diversity of many potential applications results from their unique physicochemical features. For example, high thermal stability, low vapor pressure, ability to dissolve a wide range of chemicals compounds, and the good biodegradability. This properties make ILs perfect organic solvents. Moreover, due to the ionic nature, ILs have special electrochemical properties such as a wide range of conductivity (0.1–18 mS/cm) that combined with broad electrochemical window makes them a strong candidate for applications in electrochemistry. For instance, in batteries ILs become an alternative to traditional carbonate-based electrolytes and another very promising possibility is the potential usage of ILs as double-layer capacitors (EDLC). In the view of these electric device applications, the conductivity of ionic liquids and their temperature dependence are of the great importance.

In our study, we focus on verifying the proportionality between Eact and Vact for ordinary aprotic ionic liquid [C8MIM][NTf2] (1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide). The direct analysis of isothermal and isobaric dc-conductivity data collected for classical ionic liquid clearly shows that at ambient pressure conditions the dynamic modulus (M) is constant.[1,2] Subsequently, we strive to predict the new physical quantity - M - by taking advantage of T-V version of Avramov entropic model. We demonstrate that the dynamic modulus can be defined by means of thermodynamic quantities, i.e. isothermal compressibility and thermal expansion coefficient. From this point of view new connection between thermodynamic and dynamic properties of supercooled liquids, being an alternative to density scaling idea, is provided.

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Self-diffusion and Li$^+$-ion conduction in succinonitrile-based plastic-crystalline electrolytes

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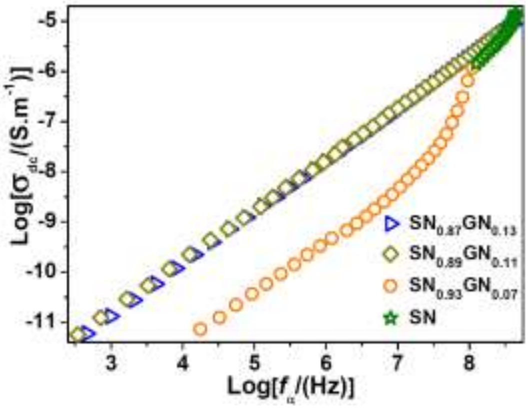
Plastic-crystalline ionic conductors have been the subject of intensive research due to their applications in electrochemical and photovoltaic devices such as fuel cells, batteries, supercapacitors, and solar cells. Here, we use temperature-dependent dielectric spectroscopy and calorimetry to probe the phase behavior, molecular dynamics, and charge conduction properties of organic plastic-crystal electrolytes made of binary co-crystals of succinonitrile (SN, $N{\equiv}C–(CH_2)_2–C{\equiv}N$) with low molar fractions of glutaronitrile (GN, $N{\equiv}C–(CH_2)_3–C{\equiv}N$). Succinonitrile displays a plastic-crystalline phase that behaves as a solid ion or proton conductor in the presence of ionic impurities or when doped with acids or lithium salts, suggesting a possible application as plastic electrolyte.[1] We find that the Sn-rich SN-GN co-crystals represent the first-ever-known plastic crystals to display a perfect correlation between the ion drift and the on-site reorientational dynamics. As shown in the figure, the samples obey the Walden and Stokes-Einstein rules typical of ideal liquid electrolytes, implying also that an effective viscosity against diffusion can be defined for this plastic-crystal phase.[2,3]

These surprising results, never reported before in an ordered solid, are interpreted in terms of a perfect correlation between the time scale of translational diffusion and that of purely reorientational on-site dynamics, which is reminiscent of the similar relaxation timescales of ethanol in its supercooled liquid and plastic-crystalline phases.[4,5,6] Doping the SN-GN co-crystals with lithium salts boosts the conductivity but breaks such perfect correlation, which indicates that the rotation-drift correlation is only valid when charge transport is dominated by self-diffusion of molecular ions intrinsic to SN or GN, while the motion of smaller atomic (Li$^+$) ions is decoupled from the molecular dynamics. This finding can be rationalized assuming that the intrinsic dc conductivity is due to self-diffusion of a minority of ionized dinitrile molecules.



Dc conductivity (σ_{dc}) *vs* primary relaxation frequency (f_α) for different SN-GN co-crystals.

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Large polaron conductivity in manganese borosilicate glass

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A new material, borosilicate glass containing high amount of MnO (60MnO-xSiO$_2$-(40-x)B$_2$O$_3$, x = 5, 10, 15, 20 and 30), was obtained and examined. According to large polaron theory [1, 2], a concentration of transition metal ions at different oxidation levels and a mean distance between them have a high influence on conductivity.

On the basis on UV-Visible absorption spectroscopy and XPS measurements, we suggest that the Mn is present mainly at second oxidation level, but increasing of SiO_2 causes a slight shift of mean oxidation level toward a higher value.

The impedance spectroscopy measurements revealed that ac and dc conductivity of the glass increases with increase in SiO_2 content, as we believe, mainly as an effect of a decrease in mean distance between manganese ions. Length of polaron radius were measured as similar to mean distance between manganese ions in Mn_2O_3, what suggest that polarons are centred on Mn^{3+} ions. An activation energy of conductivity was higher than observed in typical polaron hopping conductors, but decreases with increase in a concentration of Mn ions, as an effect of decreasing distance between transition metal ions.

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Conductivity in nematic liquid crystals: Nematic order, ionic concentrations and mobilities

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The study of dielectric properties of nematic liquid crystals (NLC), e.g. the conductivity mechanism, is of great importance for applications like NLC diplays. Generally for displays NLC-mixtures are used nowadays to achieve high performance. One of the key challenges avoiding defects in displays (like the so-called image sticking or other phenomena) is to minimize and understand conductivity in NLCs. Mainly, conductivity in LCs or their finite resistance comes from ionic impurities dissolved in the medium. Besides ionic mobility and concentration, the order parameter plays a major role and can remarkably change the ionic mobility.

We present typical dielectric spectra for the LC mixture E7 and analyze the complex dielectric function and conductivity concerning temperature and alignment (parallel and vertical with respect to the electric field). We focus on the analysis of ionic mobility and concentration that we extract from experimental data by the application of different models based on continuity equations or Poisson-Nernst-Planck (PNP) approaches [2-6]. Furtheron, we discuss results obtained with these models with respect to the applicability on NLCs.

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Elucidating the effect of affinity and association on ion transport in polymeric desalination membranes using electrochemical impedance spectroscopy

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A widespread approach used in current desalination models is to link equilibrium partitioning at the two membrane interfaces (or at the pore entry and exit) to the transport within the homogeneous pores matrix, described by the so-called extended Nernst–Planck equation. Partitioning relations are presently described by a combination of Steric, Donnan, and diElectric exclusion (SDE model). However, filtration data and other independent measurements of ion partitioning indicate that SDE model is not consistent with experiment and fail to predict membrane performance for different salts and concentrations.

In order to understand the deviation form SDE exclusion model, we carry out a systematic quantitative examination of ion transport in the active layer of different polymeric membranes using impedance spectroscopy (EIS). By varying the salt type, concentration pH, and membrane type the observed trends may be compared to the SDE predictions and other available data to gain new insights into the nature of ion permeation in desalination membranes.

EIS experiments with single salt solutions clearly show deviations from the standard model. For instance, the fixed charged in reverse osmosis membranes does have a strong impact on the ion permeability, but the impact is significantly lower than the expected from the standard model. These and other results may be explained by the non-homogeneity of reverse osmosis membranes, acting as randomly connected regions of polyamide with a wide distribution of density and charge. Results also point to an exceptionally high affinity of polyamide to protons, which exceeds that of common inorganic ions by several orders of magnitude and gives to unusual concentration dependence of impedance. These and other data are discussed and rationalized using a new picture of ion exclusion and transport in desalination polymers.

Boundary conditions at electrode - ionic liquid interface for dielectric spectroscopy measurements

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The phenomena occurring at the interface between the electrodes and a liquid with ionic conductivity is manifested specifically in the spectrum of the dielectric permittivity. The theory presented here describes the drift, diffusion, generation-recombination phenomena that occur in the sample volume and the charge transfer and adsorption-desorption processes at the metal electrode-ionic liquid interface.

The electrodes are conductors. A pair of ions with equal and opposite charge is considered. We propose general boundary conditions (BCs) with charge transfer current which contains the adsorption-desorption parameters [1]. The BCs and the basic equations of the Poisson-Nernst-Planck model are re-formulated through new variables. The mathematical problem is solved analytically. With compact formula for admittance (or permittivity) we can make a unified analysis of the various particular cases of interest encountered both in literature and in practice. The model can be extended to the case in which the ions have finite dimensions by considering the compact layer. The accumulation of ions at the electrodes is inevitable as the mobile electric charge carriers cannot pass through the separating surface between sample and electrodes. If the electrodes are non-blocking, the electric current density has a conduction component due to the charge transfer across the surface of the electrode. The charge transfer between the sample and the external circuit can be expressed in several ways [2,3]. According to the Chang-Jaffe model [4,5,6], the ionic current is proportional to the excess of ion concentrations in front of the electrode $j_\eta(\pm L/2,t) = \pm q_\eta S_\eta\left[\eta(\pm L/2,t) - \eta_{eq}\right]$; $\eta = p,n$. Another, called ohmic electrodes model [2,3] assumed that ionic current density at electrodes is proportional to the surface electric field $j_\eta(\pm L/2,t) = \pm q_\eta K_\eta E_1(\pm L/2,t)$. Because the ions cannot cross the surface, the electric current densities have two components: a component of the carrier concentrations variation and a component of the electric charge transferred from ions to the external circuit. It will be presented the steps to establish generalized boundary conditions [1]: for $x = \pm L/2$

$$J_p(x) = \pm V_p\left(p(x) - p_{eq}\right) + K_p\left(E(x) - E_{eq}\right), \qquad J_n x = \pm V_n\left(n(x) - n_{eq}\right) - K_n\left(E(x) - E_{eq}\right).$$

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How Is Charge Transport Different in Ionic Liquids? : The Role of High Pressure

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Arguably, the understanding of ion relaxation and diffusion in interacting or cooperatively relaxing systems remains the major physical quest in material chemistry. In this context, fluid consists solely of ions, such as ionic liquids (ILs), show unique properties compared to the liquids whose molecular components are neutral, and exhibit a melting point, T_m or glass transition, T_g below ~ 100 °C. The cations are generally an organic structure of low symmetry whereas the anions are inorganic or organic compounds that have a diffuse or protected negative charge. The vast majority of ILs incorporate cations of unitary charge that are created from a neutral substrate by the net addition of H^+ or R^+ to a heteroatom lone pair, where the heteroatom is the incipient cation molecular structure. Those ILs arising from the addition of H^+ are called 'protic' ILs (PILs), while their R^+ counterparts are deemed to be 'aprotic' (AILs). The major difference between PILs and other ILs is the presence of this exchangeable proton. Intriguingly, this can produce hydrogen bonding between acid and base and in some cases an H-bonded extended network. These features may together result in an exceptionally high ionic conductivity of protic ionic systems in anhydrous conditions and thus make them suitable candidates for functional applications in energy storage and electrochemical devices. In order to properly utilize these ILs in the most efficient manner, at this juncture, it is critical to understand the transport properties that govern the behavior of these materials at various thermodynamic conditions. One of these properties of ILs is ionic conductivity which depends on ion type, size, charge, temperature and pressure. Thus, in the last few years many efforts have been devoted to comprehend the behavior of conductivity relaxation in ILs at various thermodynamic conditions. However, our goal in this presentation is to provide a new perspective of the molecular dynamics of conductivity relaxation process at elevated pressure conditions which is unusual in literature.

The structure-property relationship in ILs is largely determined by a combination of long-range Coulombic forces, hydrogen-bonding interactions, and packing factors. Literature reports that the ILs are liquid because they do not pack well. As the thermodynamic variable pressure acts directly on the molecular packing thus perturbs intermolecular interaction. As a consequence, the difference in transport properties such as conductivity behavior between PIL and AIL can be suitably resoluted. A key family of ILs still generating a lot of interest is based on the imidazolium structure because ease of property tunability. The focus of attention in this work is to examine the transport properties of the following ionic liquids $[C_4Him][NTf_2]$, $[C_4Him][HSO_4]$ and $[C_4mim][NTf_2]$ at high pressure using broadband dielectric spectroscopy. This concerted approach allows a more detailed analysis to understand the role of activation volume that distinguishes the protic from aprotic ionic liquids.

Structure and electrical properties of segregated polymer composites

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Conductive polymer composites play important role in various areas of electronic industry due to their distinguished properties. Most of such composites are polymer matrix (thermoplastic or thermoset) that provides mechanical properties containing conductive fillers (carbon, metallic, ceramic) which impart needed electrical characteristics. However, conductive polymer composites with random distribution of conductive particles within polymer matrix require quite high values of filler content to achieve high conductivity. While such high filler content can significantly damage the mechanical properties and manufacturing processes.

Segregated polymer composites (SPC) can be a good solution to overcome this problem. In SPC conductive filler creates an ordered framework in polymer matrix. The local concentration of filler φ_{loc} in the wall of SPC framework is higher than mean filler concentration φ calculated for the whole volume of sample, $\varphi_{loc} > \varphi$. Owing to this the percolation threshold φ_c, defining the insulator/conductor transition, is much lower than for the random distribution of filler. Mechanical mixture of polymer and filler powders with size of particles $d_{pol} >> d_{fil}$ under hot compacting forms the ordered segregated structure where conductive filler particles are located on the boundaries of polymer grains.

For our research, we used the ultra-high-molecular-weight polyethylene (UHMWPE) with d_{pol}=100 µm and the thermally treated anthracite as a conductive filler due to its close nature to graphene properties. In parallel there were produced the composites based on polypropylene (PP) and epoxy resin (EP) with random distribution of anthracite filler.

Obtained results show that filler concentration dependence of conductivity obeys a known percolation equation $\sigma=\sigma_0(\varphi - \varphi_c)^t$ for all systems. The value of percolation threshold for SPS is φ_c=0.029 while for randomly distribute anthracite φ_c=0.25. Electron transport through the conductive framework provides relatively high level of conductivity in SPC.

Segregated systems with anthracite filler are promising as a base for the future applications, for example as EMI shielding material, different sensors, etc.

Solid polymer electrolyte composites based on epoxy oligomer and lithium perchlorate salt: thermal characteristics, ion-conductivity and permittivity

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It is a common knowledge that the polyethylene oxide (PEO) has a significant ability to solvate the alkali metal salts, a low lattice energy and, as a consequence on its basis, it is the presence of high ionic conductivity (above the melting temperature, when it is not in the crystalline state) in materials. The choice of the epoxy oligomer of diglycide aliphatic ester of polyethylene glycol (DEG) was justified by its chain structure that is similar to the PEO, but it is amorphous.

In the present study the epoxy oligomer DEG, an epoxy-dian resin (ED-20) and the lithium perchlorate salt $LiClO_4$ were used for synthesis of ion-conductive epoxy polymer composites. DEG-ED-$LiClO_4$ solutions were respectively prepared with content from 0 to 30 phr of lithium perchlorate salt on 30/50/70 phr of DEG and 70/50/30 phr of ED. Polyethylene polyamine hardener (PEPA) was used as a curing agent. The content of PEPA was 10 phr for all cases.

Thermal characteristics have been studied by differential scanning calorimetry in the temperature range from -70 to +200 °C with a heating rate of 10 °C/min. The increasing of $LiClO_4$ content from 0 to 30 phr leads to the rise of glass transition temperature of the obtained polymers from +7 to +65 ºC (DEG(70 phr)- ED(30 phr)), from +40 to +103 °C (DEG(50 phr)- ED(50 phr)) and from +89 to +149 ºC (DEG(30 phr)-ED(70 phr). It is shown that the salt affects on structure of the polymer.

Dielectric studies of the synthesized composites have been carried out using broadband dielectric spectroscopy in the frequency range 10^{-1}-10^{7} Hz and the temperature range from -60 to +200 °C. It was found that the ionic conductivity increased with the addition of lithium perchlorate salt due to the increase of the charge carrier amount up to an optimum value. The highest ionic conductivity σ' and the permittivity ε' were $5{\cdot}10^{-5}$ S/cm and $2{,}9{\cdot}10^{4}$ (at 10^{3} Hz), respectively, for the composite with 30 phr of $LiClO_4$ in DEG(30 phr)-ED(70 phr) system at 200 °C.

According to the thermogravimetric analysis results, the weight loss at 200 is negligible, that indicates its usability at elevated temperatures. Structural organization and features of macromolecular ordering of the synthesized polymer systems were investigated by wide-angle X-ray scattering. Analysis showed that all systems are amorphous.

Towards Microvolume Dielectric Spectroscopy of Biomolecules

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To study the dynamics and electrical properties of biomolecules, we have designed and fabricated grounded coplanar waveguide-based chip for dielectric spectroscopy of liquids in 1-50 GHz band and implemented a method for the permittivity extraction based purely on the extraction from measured scattering parameters. To our knowledge, the proposed bio sensing method represents an advantage to the current known sensors because the dielectric function of sample is obtained purely by using precision calibration techniques and computational optimization without any *a priori* assumption about the dielectric model of measured sample. This sensor is also designed with well defined low-volume active area to achieve the high sensitivity to dielectric change which associated to its size permits to work with microvolume (few hundred microliters) liquid samples. In the pioneering experiments we were interested in dielectric (i.e. polarization) properties of various amino acid solutions. The polar nature of amino acids determines their behavior in aqueous solutions and due to fact that at least one relaxation process is anticipated in microwave band, it allows us to study their dynamics and structure by using broadband dielectric spectroscopy. Data extracted from experiment are in an exact agreement in comparison with widely used reflection method by coaxial probe and shows the shift of relaxation times and also the trend of rising static permittivity at low frequencies with rising concentration of amino acids.

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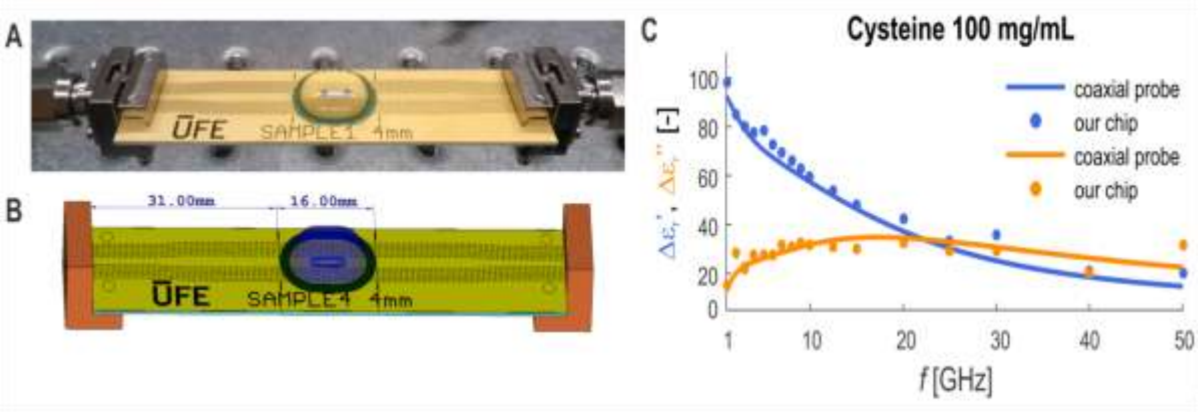

Fig. A) Fabricated chip with a 250 µL sample. B) CST Microwave studio model of grounded coplanar waveguide chip. C) Reference data obtained using commercial coaxial method (85070E Dielectric Probe Kit - Keysight Technologies, 5 mL sample) vs. data from our chip (points).

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