

Online IDS 2020 Workshop



International Dielectric Society

Organizer: Ranko Richert

Advisory team: Catalin Gainaru, Alexei Sokolov

Workshop dates: **September 28 - September 30, 2020**

Talks: **Monday, September 28: 15:00 - 17:30, break, 18:30 - 21:00,**

Tuesday, September 29: 15:00 - 17:30, break, 18:30 - 21:00

Wednesday, September 30: 15:00 - 17:30, break, 18:30 - 20:30

Times are based on **Central European Summer Time (CEST) = UTC + 2.**

(Central European Time (CET) + daylight saving time, local time in Brussels)

Talks are **30 minutes each (20 talk + 10 min discussion)** in licensed **Zoom** room.



Program Overview: 27 talks

MONDAY	SEP 28	15:00 - 17:30	Dielectric Topics
15:00	<i>Introduction</i>		
15:30	Kristine Niss	<i>Long-time structural relaxation of glass-forming liquids: Simple ...</i>	
16:00	Riccardo Casalini	<i>Temperature and volume dependence of the dielectric relaxation ...</i>	
16:30	Silvina Cervený	<i>Isotope effect on the dynamics of hydrophilic solutions at supercooled ...</i>	
17:00	Dmitry Bedrov	<i>How efficient is Li^+ ion transport in solvate ionic liquids: Insight ...</i>	
MONDAY	SEP 28	18:30 - 21:00	Ionic Liquids / Conductivity
18:30	Catalin Gainaru	<i>Electric conductivity concepts describing the generic rheological ...</i>	
19:00	Alexei Sokolov	<i>Strongly correlated ion dynamics in concentrated ionic systems</i>	
19:30	Bernhard Roling	<i>Ion correlations in high concentrated liquid electrolytes</i>	
20:00	Zaneta Wojnarowska	<i>Transport properties of 1,2,3-triazolium-based poly(ionic liquid) (PIL) ...</i>	
20:30	Madalena Dionísio	<i>Using conductivity to explore the way how a guest is distributed among ...</i>	
TUESDAY	SEP 29	15:00 - 17:30	Hydrogen Bonded Systems
15:00	Yuri Feldman	<i>Water as a marker of oxygenation state in aqueous solutions of ...</i>	
15:30	Martin Tress	<i>Do hydrogen bonds undermine the link between structural ...</i>	
16:00	Silvia Arrese-Igor	<i>New insights on the dielectric relaxation of alcohols</i>	
16:30	Roland Böhmer	<i>Hyperquenched pressure-densified glycerol</i>	
17:00	Paul Ben Ishai	<i>The dielectric response of frozen food</i>	
TUESDAY	SEP 29	18:30 - 21:00	Polymers
18:30	Paulina Szymoniak	<i>Resolving a mystery of the molecular dynamics of epoxy-based ...</i>	
19:00	Michael Wübbenhorst	<i>Transient dynamics of cold-rolled atactic-polystyrene using broadband ...</i>	
19:30	Simone Napolitano	<i>Nonequilibrium dynamics of interfacial polymer layers</i>	
20:00	George Floudas	<i>Polymers under 2-D confinement: In situ polymer imbibition in nanopores</i>	
20:30	Aparna Beena-Unni	<i>The segmental dynamics of polymer films confined on a substrate</i>	
WEDNESDAY	SEP 30	15:00 - 17:30	Nano / Composites / Local
15:00	Silvia Soreto Teixeira	<i>Electrical properties of lithium ferrite/poly(lactic acid) composites</i>	
15:30	Anatoli Serghei	<i>Universal correlation between the electromagnetic interference ...</i>	
16:00	Ranko Richert	<i>Physical vapor deposition onto interdigitated electrode cells</i>	
16:30	Massimiliano Labardi	<i>Lateral resolution and spectral bandwidth of local dielectric spectroscopy</i>	
17:00	Shiwang Cheng	<i>Desorption dynamics in polymer nanocomposites through a ...</i>	
WEDNESDAY	SEP 30	18:30 - 20:30	Combining / Comparing Techniques
18:30	Ernst A. Rössler	<i>Generic structural relaxation in molecular liquids: Photon correlation ...</i>	
19:00	Joshua Sangoro	<i>Correlating microscopic heterogeneity and dynamics in deep eutectic ...</i>	
19:30	Thomas Blochowicz	<i>Universal structural relaxation in supercooled liquids and the role of ...</i>	
20:00	<i>Concluding Remarks</i>		

Online IDS 2020 Workshop: Day 1

MONDAY **SEPTEMBER 28** **15:00 - 17:30**

15:00 *Introduction*
Ranko Richert

Dielectric Topics Chair: Ranko Richert

15:30 *Long-time structural relaxation of glass-forming liquids: Simple or stretched exponential?*
Kristine Niss, J. Dyre, T. Hecksher

16:00 *Temperature and volume dependence of the dielectric relaxation in liquids and polymers*
Riccardo Casalini

16:30 *Isotope effect on the dynamics of hydrophilic solutions at supercooled temperatures*
J. H. Melillo, Silvina Cervený

17:00 *How efficient is Li^+ ion transport in solvate ionic liquids: Insight from atomistic molecular dynamics simulations*
Dmitry Bedrov

MONDAY **SEPTEMBER 28** **18:30 - 21:00**

Ionic Liquids / Conductivity Chair: Joshua Sangoro

18:30 *Electric conductivity concepts describing the generic rheological response of supercooled liquids*
P. Münzner, S. Ahlmann, A. Sokolov, R. Böhmer, Catalin Gainaru

19:00 *Strongly correlated ion dynamics in concentrated ionic systems*
Alexei Sokolov

19:30 *Ion correlations in high concentrated liquid electrolytes*
Bernhard Roling

20:00 *Transport properties of 1,2,3-triazolium-based poly(ionic liquid) (PIL) at ambient and elevated pressure*
Zaneta Wojnarowska, M. Musiał, S. Cheng, M. Paluch

20:30 *Using conductivity to explore the way how a guest is distributed among a nanoporous host*
Madalena Dionísio

Online IDS 2020 Workshop: Day 2

TUESDAY

SEPTEMBER 29

15:00 - 17:30

Hydrogen Bonded Systems

Chair: Catalin Gainaru

15:00 *Water as a marker of oxygenation state in aqueous solutions of hemoglobin: Microwave dielectric study*

Yuri Feldman, L. Latypova, G. Barshtein, A. Puzenko, Y. Poluektov, A. Anashkina, I. Petrushanko, S. Fenk, A. Bogdanova

15:30 *Do hydrogen bonds undermine the link between structural relaxation and density?*
Martin Tress

16:00 *New insights on the dielectric relaxation of alcohols*
Silvia Arrese-Igor

16:30 *Hyperquenched pressure-densified glycerol*
C. Gainaru, H. Nelson, J. Huebinger, M. Grabenbauer, Roland Böhmer

17:00 *The dielectric response of frozen food*
Paul Ben Ishai, A. Greenbaum (Gutina), I. Lunev, Y. Feldman

TUESDAY

SEPTEMBER 29

18:30 - 21:00

Polymers

Chair: Ernst Rössler

18:30 *Resolving a mystery of the molecular dynamics of epoxy-based materials using broadband dielectric spectroscopy and hyphenated calorimetry*
Paulina Szymoniak, H. Omar, X. Qu, A. Schönhals

19:00 *Transient dynamics of cold-rolled atactic-polystyrene using broadband dielectric spectroscopy*
Michael Wübbenhorst

19:30 *Nonequilibrium dynamics of interfacial polymer layers*
Simone Napolitano

20:00 *Polymers under 2-D confinement: In situ polymer imbibition in nanopores*
George Floudas, C.-H. Tu

20:30 *The segmental dynamics of polymer films confined on a substrate*
Aparna Beena Unni, K. Chat, K. Balin, D. M. Duarte, M. Wojtyniak, M. Geppert-Rybczyńska, J. Kubacki, R. Wrzalik, R. Richert, K. Adrjanowicz

Online IDS 2020 Workshop: Day 3

WEDNESDAY SEPTEMBER 30

15:00 - 17:30

Nano / Composites / Local

Chair: Alexei Sokolov

- 15:00** *Electrical properties of lithium ferrite/poly(lactic acid) composites*
Silvia Soreto Teixeira, N. Gama, T. Cordeiro, M. P. F. Graça, A. Barros-Timmons, M. Dionísio, L. C. Costa
- 15:30** *Universal correlation between the electromagnetic interference shielding effectiveness of composite materials and their spectroscopic electrical impedance*
Anatoli Serghei
- 16:00** *Physical vapor deposition onto interdigitated electrode cells*
Ranko Richert
- 16:30** *Lateral resolution and spectral bandwidth of local dielectric spectroscopy*
Massimiliano Labardi, R. Casalini, S. Capaccioli
- 17:00** *Desorption dynamics in polymer nanocomposites through a combination of dielectric spectroscopy and rheology*
Shiwang Cheng

WEDNESDAY SEPTEMBER 30

18:30 - 20:30

Combining / Comparing Techniques

Chair: Martin Tress

- 18:30** *Generic structural relaxation in molecular liquids: Photon correlation and NMR spectroscopy vs dielectric spectroscopy*
T. Körber, R. Stäglich, C. Gainaru, R. Böhmer, Ernst A. Rössler
- 19:00** *Correlating microscopic heterogeneity and dynamics in deep eutectic solvents*
Joshua Sangoro
- 19:30** *Universal structural relaxation in supercooled liquids and the role of cross-correlations in dielectric spectroscopy*
Thomas Blochowicz
- 20:00** *Concluding Remarks*
Ranko Richert

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Long-time structural relaxation of glass-forming liquids: Simple or stretched exponential?

Kristine Niss, Jeppe Dyre and Tina Hecksher

Department of Science and Environment, Roskilde University, Denmark

In the context of viscous liquids and the glass transition, the stretched-exponential function is the standard function used to describe data because it often provides a better fit than other single-shape-parameter functions. In the last 30 years, numerous papers have reported dielectric spectra for glass-forming liquids fitted to the Laplace transform of the stretched exponential. The Laplace transform of the stretched exponential displays the characteristic asymmetric loss peak with an approximate power-law decay above the loss-peak frequency and an asymptotic slope unity (in a log–log plot) increase in the loss below the loss-peak frequency. The focus in this work is on the region below the loss peak, i.e. the long time limiting behaviour of the relaxation. There is a rapid decay of the relaxation-time distribution at long times if the stretched exponential is written as a sum of exponentials, but there is no terminal longest relaxation time for a stretched exponential. We address the question of whether the relaxation data complies to this feature of the stretched exponential or whether there is an effective cutoff at a “terminal” (longest) relaxation time? The latter situation yields exponential relaxation as the limiting long time behavior.

We present volume relaxation data on squalane close to the glass transition temperature measured with dielectric dilatometry [1]. The volume relaxation is monitored after a temperature steps of sizes from 0.12 K to 1.65 K leading to linear-response relaxation and non-linear aging respectively [2]. The linear-response relaxation function is extracted from the aging data by invoking the single-parameter-aging scenario [3,4] and scaling the aging data onto the linear relaxation data as in Ref. 5. The linearized aging data has higher resolution than the directly measured linear data and allows for a detailed study of the long time behaviour of the relaxation function.

Based on the linearized aging data of squalane, we show that the volume relaxation toward equilibrium in fact follows a simple exponential function at long times; a stretched-exponential function provides a poor fit. This demonstrates the existence of a terminal relaxation rate for the volume relaxation, corresponding to an effective long-time cutoff in the spectrum of structural relaxation times.

[1] Niss et al., Phys. Rev. E. **85**, 016313 (2012).

[2] Niss et. al., J. Chem. Phys. **152**, 041103 (2020).

[3] Hecksher et al., J. Chem. Phys. **142**, 241103 (2015).

[4] Hecksher et al., Proc. Natl. Acad. Sci. U. S. A. **116**, 16736–16741 (2019).

[5] Niss, Phys. Rev. Lett. **119** 115703 (2017).

Temperature and volume dependence of the relaxation time in liquids and polymers: Is the thermodynamical scaling exponent γ constant?

R. Casalini

Naval Research Laboratory, Chemistry Division, Washington DC 20375-5342, USA.

Since its initial discovery more than fifteen years ago, the thermodynamical scaling of the dynamics of supercooled liquids has been used to provide many new important insights in the physics of liquids, particularly on the link between dynamics and intermolecular potential. A question that has long been discussed is whether the scaling exponent γ_s is a constant or does it depends on pressure. An alternative definition of the scaling parameter, $\eta = \partial \ln T / \partial \ln \rho_x$ has been presented in the literature, and has been erroneously considered equivalent to γ_s . Here we offer a simple method to determine the pressure dependence of η using only the pressure dependence of the glass transition and the equation of state.

Using this new method we find that for nonassociated liquids investigated, η always decreases with increasing pressure. Importantly in all cases the value of η remains always larger than 4. Liquids having η closer to 4 at low pressure show a smaller change in η with pressure. While for associated liquids η always increases with increasing pressure, while remaining always smaller than 4. We argue that this result has very important consequences for the experimental determination of the functional form of the repulsive part of the potential in liquids.

Comparing the pressure and temperature dependence of γ_s and η we find, contrary to what has been assumed in the literature to date, that these two parameters are not equivalent and have very different pressure and temperature dependences.

Isotope effect on the dynamics of hydrophilic solutions at supercooled temperatures

Jorge H. Melillo¹, Silvina Cervený^{1,2*}

¹*Centro de Física de Materiales (CSIC-UPV/EHU)-Material Physics Centre (MPC), Paseo Manuel de Lardizábal 5 (20018), San Sebastián, Spain.*

²*Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4 (20018), San Sebastián, Spain.*

*email: silvina.cervený@ehu.es

Numerous works have been done in the last years concerning the dynamics of water in hydrophilic solutions at supercooled temperatures using broadband dielectric spectroscopy^{1, 2}. However, there are some effects on water dynamics that were not explored in detail. In particular, in this talk, we will analyze the isotope effects on the dynamics of water in these solutions. The solutes used were tri-propylene glycol (3PG), penta-ethylene glycol (5EG) and 1-lysine in solution with three isotopes of water (H_2O , D_2O and H_2^{18}O). Using these three isotopes, we can access the effects of mass and moment of inertia as well as the impact of nuclear quantum effects (NQEs) on the dynamics of water in hydrophilic solutions. We found that nuclear quantum effects are more relevant than mass effects at both high water contents and low temperatures.

1. Swenson, J.; Cervený, S., Dynamics of Deeply Supercooled Interfacial Water. *J. Phys.: Condens. Matter* **2015**, 27, 033102.
2. Cervený, S.; Mallamace, F.; Swenson, J.; Vogel, M.; Xu, L., Confined Water as Model of Supercooled Water. *Chemical Reviews* **2016**, 116 (13), 7608-7625.

How efficient is Li⁺ ion transport in solvate ionic liquids: Insight from atomistic molecular dynamics simulations.

Dmitry Bedrov

*Department of Materials Science & Engineering, University of Utah, 122 South Central Campus Drive,
Room 304, Salt Lake City, Utah 84112, United States*

The complex interplay between the local structure and dynamic correlations in bulk electrolytes are among key issues that define efficiency of Li-ion batteries and other energy storage devices. These correlations require further comprehension and understanding, particularly at molecular scale. In this talk, we will discuss how the atomistic molecular dynamics simulations can provide a valuable insight into understanding the mechanisms and correlations of ion motion in various environments. Specifically, we will discuss Li⁺ transport in solvate ionic liquids (SILs) comprised of Li-bis(trifluoromethyl)phosphine sulfide (TFSI) salt/tetraglyme mixtures in light of experimental analysis based on very-low-frequency impedance spectra and the Onsager reciprocal relations. SILs comprised of an equimolar mixture of a lithium salt with glyme molecules are considered as a promising class of highly concentrated electrolytes for future Li-ion batteries. Both simulations and experiments on this mixture show that while the ionic conductivity and the Li⁺ transport number are quite high, the Li⁺ transference number under ‘anion-blocking conditions’ is extremely low, making these electrolytes rather inefficient for battery applications. The contribution of cation-anion correlation to the total ionic conductivity is highly positive due to strongly anti-correlated cation-anion motions. Such cation-anion anti-correlations have also been found in standard ionic liquids and are a consequence of the constraint of momentum conservation. The molecular origin of low Li⁺ transference number and the influence of anti-correlated motions on Li⁺ transport efficiency have been investigated as a function of solvent composition. We demonstrate that Li⁺ transference number can be increased either by reducing the residence time between Li⁺ and solvent molecules or by adding excessive solvent molecules that are not complexing with Li⁺.

Electric conductivity concepts describing the generic rheological response of supercooled liquids

P. Münzner,¹ S. Ahlmann,¹ A. Sokolov,² R. Böhmer,¹ Catalin Gainaru¹

¹*Fakultät Physik, Technische Universität Dortmund, 44221 Dortmund, Germany*

²*Department of Chemistry, University of Tennessee, Knoxville, and Oak Ridge National Laboratory, TN, USA*

Two recent surveys of shear oscillatory data acquired for a large variety of viscous materials reveal a remarkable simplicity with respect to the spectral signatures of their structural rearrangements [1,2]. This lack of material individualities prevails when the mechanical data are presented in terms of fluidity and resembles the so-called “first universality” discussed in relation with the (electric) conductivity response of ionic conductors [3]. Exploiting this analogy, we successfully adopted several concepts widely used for the description of the charge transport to its rheological, hence molecular flow-related, counterpart [4,5,6]. Regarded in susceptibility terms, this rheological simplicity is also shared by the reorientation dynamics probed by nuclear magnetic resonance, light scattering, and, under certain circumstances, dielectric spectroscopy [2]. In our view, the present results significantly broaden the perspective in which the microscopic dynamics in disordered materials should be regarded.

- [1] S.P. Bierwirth, R. Böhmer, and C. Gainaru, Phys. Rev. Lett. 119, 248001 (2017)
- [2] C. Gainaru, Phys. Rev. E 100, 020601(R) (2019)
- [3] K. Funke, R.D. Banhatti, L.G. Badr, D.M. Laughman, and H. Jain, J. Electroceram. 34, 4 (2015)
- [4] P. Münzner, L. Hoffmann, R. Böhmer, and C. Gainaru, J. Chem. Phys. 150, 234505 (2019)
- [5] F. Wieland, V. Bocharova, P. Münzner, W. Hiller, R. Sakrowski, C. Sternemann, R. Böhmer, A.P. Sokolov, and C. Gainaru, J. Chem. Phys. 151, 034903 (2019).
- [6] C.A. Thomann, P. Münzner, K. Moch, J. Jacquemin, P. Goodrich, A.P. Sokolov, R. Böhmer, and C. Gainaru, submitted to J. Chem. Phys. (2020)

Strongly Correlated Ion Dynamics in Concentrated Ionic Systems

Alexei P. Sokolov

University of Tennessee and Oak Ridge National Laboratory, TN, USA

Understanding the mechanisms controlling ionic conductivity is critical for many technologies, and most of the studies are focused on ion diffusion. In this contribution we discuss the significant role played by ionic correlations in conductivity of concentrated ionic systems. We demonstrate that the correlations in ion dynamics reduce ionic conductivity by ~ 2 -3 times in ionic liquids (ILs), by more than 10 times in polymerized ionic liquids (PolyILs), and by almost 100 times in organic ionic plastic crystal (OIPC) [1]. This is in contrast to superionic ceramics, where correlations enhance ionic conductivity by ~ 3 -5 times. Thus, ionic correlations, usually neglected in many studies, play a very important role in conductivity of concentrated ionic systems. These results cannot be explained by a diffusion of ion pairs because PolyILs and OIPC are essentially single ion conductors. In contrast, strongly correlated motions of mobile ions with the same charge (cation-cation or anion-anion correlations) are the major mechanism suppressing the ionic conductivity in these systems. Based on these results we emphasize that charge transport rather than ion diffusion is critical for electrolyte performance, and suggest potential design of plastic crystals and polymer electrolytes with enhanced ionic conductivity.

1. I. Popov, et al., **J. Phys. Chem. C** **124**, 17889-17896 (2020).

Ion correlations in high concentrated liquid electrolytes

Bernhard Roling

Department of Chemistry, University of Marburg, Hans-Meerwein-Strasse 4, 35032 Marburg, Germany

Highly concentrated electrolytes, like ionic liquids, solvent-in-salt electrolytes, and solvate ionic liquids, exhibit low vapor pressures and are non-flammable. Therefore, they are promising materials for the development of safe battery systems for mobile and stationary applications. Due to the high ion concentrations in these electrolytes, strong ionic interactions lead to complex ion transport mechanisms and to strongly correlated movements of the ions. For electrolyte with a single type of cations and a single type of anions, the transport properties are completely described by five transport coefficients and one thermodynamic factor. Consequently, six measurable quantities are needed for a complete experimental characterization of the ion transport.

In this presentation, methods for this complete experimental characterization will be described, and the physical meaning of obtained transport coefficients in terms of ion correlations will be discussed [1-2]. The impact of ion correlations on the transport in batteries will be explained [3-4].

- [1] F. Wohde, M. Balabajew, B. Roling, J. Electrochem. Soc. 163 (2016) A714-A721.
- [2] D. Dong, F. Sälzer, B. Roling, D. Bedrov, Phys. Chem. Chem. Phys. 20 (2018) 29174-29183
- [3] M. Cronau, M. Kroll, M. Szabo, F. Sälzer, B. Roling, Batteries & Supercaps 3 (2020) 611-618.
- [4] N. M. Vargas-Barbosa, B. Roling, ChemElectroChem 7 (2020) 367-385.

Transport properties of 1,2,3-triazolium-based poly(ionic liquid) (PIL) at ambient and elevated pressure

Z. Wojnarowska^{1*}, M. Musiał¹, S. Cheng¹, E. Drockenmüller², M. Paluch¹

¹*Institute of Physics, University of Silesia in Katowice, Silesian Center for Education and Interdisciplinary Research, 75 Pułku Piechoty 1A, 41–500 Chorzów, Poland*

²*Univ Lyon, Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR 5223, F-69003, Lyon, France*

* zaneta.wojnarowska@smcebi.edu.pl

Polymerized ionic liquids (PILs) are a relatively new class of materials, however, already being of great interest in the fields of research and modern technologies. Such huge attention of scientific and industrial communities comes from their multiple applications as sorbents, dispersants, carbon precursors and electrolytes in various electrochemical devices, from batteries to fuel cells. Nevertheless, to design any process involving polymerized ionic conductors on an industrial scale, it is necessary to know their physical properties, such as viscosity and electric conductivity, at various T-P thermodynamic conditions.

In this talk, we present the transport properties of the 1,2,3-triazolium-based PIL in the region covering supercooled liquid and glassy states both at ambient and elevated pressure. The analysis of ambient pressure dielectric and rheological data recorded in the supercooled liquid state ($T > T_g$) revealed a strong coupling between viscosity, segmental dynamics and dc-conductivity (σ_{dc}) in studied PIL. On the other hand, two fast secondary relaxations appear in the dielectric spectra of glassy state. We found that the mobility manifested by a β -secondary process promotes segmental dynamics and thereby is responsible for fast charge transport in examined PIL. The molecular mechanism underlying such relaxation suggests a new promising paradigm for the development of PILs with enhanced ionic conductivity. Additionally, we found that isothermal and isobaric conductivity measurements analyzed in T-P-V plane give a unique possibility to estimate the critical thermodynamic (isothermal compressibility, thermal expansion coefficient) properties as well as to predict the viscosity behavior of PIL at elevated pressure

Using conductivity to explore the way how a guest is distributed among a nanoporous host

Piedade d'Orey¹, Teresa Cordeiro¹, Mirtha A. O. Lourenço^{2,3}, Inês Matos¹, Florence Danède², João C. Sotomayor¹, Isabel M. Fonseca¹, Paula Ferreira², Natália T. Correia⁴, Madalena Dionísio^{1*}

¹ LAQV-REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia – Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal;

² CICECO, Department of Materials and Ceramic Engineering, University of Aveiro, Campus Universitário de Santiago, 810-193 Aveiro, Portugal;

³ Istituto Italiano di Tecnologia - IIT, Centre for Sustainable Future Technologies (CSFT), Via Livorno 60, 10144-Torino, Italy

⁴ Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

E-mail addresses: madalena.dionisio@fct.unl.pt

To correlate the release profile of a drug with factors such as mobility within the pores, physical state and the way how it is distributed in the carrier, composites of naproxen loaded in 3 different matrices were investigated. The matrices, derived from silica, differ in the chemical composition of the pore walls and in the structural architecture, going from a disordered and 100% silica (MCM-41) matrix, passing from a partially silylated one where some methyl groups were capped by silanol moieties (MCM-41_{sil}), to a periodically ordered matrix having biphenylene moieties on the pore wall surface, PMO_{Bph}. A set of experimental techniques including attenuated full reflectance of Fourier transformed infrared spectroscopy, powder X-ray diffraction and differential scanning calorimetry were applied but special focus was given to dielectric relaxation spectroscopy. The latter allowed to characterize the amorphous fraction of naproxen within pores through the dielectric loss, while real conductivity, $\sigma'(f)$, was used to probe the crystalline fraction outside pores. The emergence of a plateau at low f , associated with the onset of dc conductivity, is observed for the three composites while approaching naproxen melting. Interestingly, in MCM-41 based composites $\sigma'(f)$ at the lowest frequencies (0.1 Hz) drops significantly with heating after naproxen's melting being overpassed ($T_{m,nap} = 156$ °C), meaning that the continuous conducting path allowing charge migration over long distances was interrupted, which is caused by the migration of liquid naproxen into the pores. In contrary, in the high hydrophobic PMO_{Bph} host, the dc plateau is always observed near T_m since naproxen recrystallizes being weakly anchored to the outer PMO_{Bph} matrix surface, and so, delivering faster to the releasing medium. Concerning the delivery behavior of the unmodified vs silylated MCM-41 matrix, the former is faster in the hydrated state, a result that is in good agreement with the mobility enhancement observed by dielectric spectroscopy. This complementary analysis provided a rational basis to understand and explain the observed drug release behavior. Moreover, the results allow concluding that all the studied composites show promising behavior as controlled drug delivery systems, and that the release profile can be tuned by both filling degree and hydration level.

Water as a marker of oxygenation state in aqueous solutions of hemoglobin: Microwave dielectric study

Yuri Feldman¹, Larisa Latypova¹, Gregory Barshtein², Anna Bogdanova³, Alexander Puzenko¹

1. *Applied Physics, The Hebrew University of Jerusalem, Jerusalem, Israel*

2. *Department of Biochemistry, The Faculty of Medicine, The Hebrew University, Jerusalem, Israel*

3. *Department Red Blood Cell Research Group, Institute of Veterinary Physiology, University of Zürich, Zurich, Switzerland*

It has become increasingly clear over the past two decades that water is not a simple solvent inevitable in living systems “life’s solvent”. Instead, it is an active player that interacts with charged groups of all the molecules, shaping tertiary and quaternary structure of proteins and controlling their properties and function [1-4]. Our recent studies using Microwave Dielectric Spectroscopy (MDS) suggested that monitoring of the dynamic balance between free and bound water gives information on deformability, longevity, and “age” of stored red blood cells (RBC) [5]. This study addresses the possible mechanisms linking the state of intracellular water and RBC deformability. Hemoglobin (Hb) is the major buffer for water in RBCs and the MDS parameters largely reflect the changes in its state and concentration in the cell. Ferrous Hb exists in two major allosteric states, tense (T) and relaxed (R) states corresponding to oxy- and deoxyhemoglobin. In this study, we have monitored the changes in relaxation peak for aqueous solutions of Hb associated with its transition from R to T state. The results are discussed in terms of Cole-Cole parameters of main water relaxation peak indicating the type of water molecules interaction (dipole-dipole/ionic dipole) during the oxygenation/oxidation transition. The number of hydrated water of Hb in its different states was compared with the results obtained by other methods.

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Do hydrogen bonds undermine the link between structural relaxation and density?

Martin Tress, Jan Gabriel, Wilhelm Kossack, and Friedrich Kremer

Leipzig University, Peter Debye Institute for Soft Matter Research, Linnestr. 5, Leipzig, 04103, Germany

Since a long time, structural relaxation in liquids is considered to be directly controlled by density. This is also the basis of most theoretical approaches to the glass transition. However, the break-down of concepts like density scaling in hydrogen bonding liquids indicates deficiencies of this link. To investigate densification on the (sub-) molecular scale and to promote an atomistic understanding of glass formation, Infrared spectroscopy is carried out on a series of polyalcohols (glycerol, threitol, xylitol, sorbitol) at temperatures ranging from far above to far below their respective calorimetric glass transition temperatures. By analyzing specific vibrations, the thermal expansion of intramolecular covalent bonds and strong intermolecular hydrogen bridges is quantitatively determined. Pronounced differences between intra- and intermolecular expansion verify the dominance of the latter. Surprisingly, the overall thermal expansion (i.e. the cube root of inverse density) is even bigger than that of the strong hydrogen bridges. This suggests that weak hydrogen bridges have a greater impact on thermal expansion while the strong hydrogen bridges clearly dominate the glass transition. These results demonstrate that inhomogeneities on intra- and intermolecular scale can play distinct roles in densification and glassy solidification.

New insights on the dielectric relaxation of alcohols

S. Arrese-Igor^a, A. Alegría^{a,b} and J. Colmenero^{a,b,c}

^a *Materials Physic Center CISC-UPV/EHU. San Sebastián, Spain.*

^b *University of the Basque Country UPV/EHU. San Sebastián, Spain.*

^c *Donostia International Physics Center. San Sebastián, Spain.*

The intriguing dielectric relaxation of monoalcohols (MA), the so-called ‘Debye’ relaxation, has been the object of numerous studies for decades [1]. In recent years there has been a substantial progress on the understanding of fundamental aspects of this process and its relation with supramolecular structures created by hydrogen bonds [1].

The starting point of the work and motivation for the research that will be presented is the puzzling discovery of up to three different timescales on the shear viscosity response of several MA [2]. The outcome of some experiments devoted to gain some knowledge on the origin on the mentioned phenomenology will be exposed. In particular, the shear and dielectric response characterization of 2-ethyl-1-hexanol (2E1H) after modifying its hydrogen bond network by the addition of small amounts of LiCl. Results will be discussed in relation to some aspects of the dielectric relaxation of MAs and, in a more general context, in relation to the dynamics of other hydrogen bonded systems.

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Hyperquenched, pressure densified glycerol

Catalin Gainaru,¹ Helge Nelson,¹ Jan Huebinger,² Markus Grabenbauer,² Roland Böhmer¹

¹ *Fakultät Physik, Technische Universität Dortmund, 44221 Dortmund, Germany*

² *Max Planck-Institut für molekulare Physiologie, 44227 Dortmund, Germany*

As reported recently in Phys. Rev. Lett. **125**, 065503 (2020), glycerol pressurized to 2 kbar and hyperquenched from the bulk liquid at rates of about -10000 K/s, has been frozen to an extreme out-of-equilibrium state. As compared to conventionally cooled melts, the resulting material exhibits lower orientational correlations, enabling the observation of a secondary relaxation peak in the ambient-pressure dielectric response. The hyperquenching rather than the pressurizing part of the preparation protocol induces the observed structural changes. These vanish entirely only well above the glass transition temperature of the equilibrium liquid and are evidence for strong similarities between hyperquenched and vapor deposited glass formers.

The dielectric response of frozen food

Paul Ben Ishai^{1*}, Anna Greenbaum (Gutina)², Ivan Lunev³, Yuri Feldman⁴

¹Dept. of Physics, Ariel University, Ariel, Israel

²Dept. of Physics, Hebrew University of Jerusalem, Jerusalem, Israel

³FRC Kazan Scientific Center of RAS, Kazan Institute of Biochemistry and Biophysics, Kazan, Russian Federation

⁴Dept. of Applied Physics, Hebrew University of Jerusalem, Jerusalem, Israel

*corresponding author: paulbi@ariel.ac.il

We have investigated the dielectric permittivity of fresh and sea water fish flesh as a function of temperature. The measured spectra are complex with many overlain interfacial processes. However, 2 distinct process related to water-protein complexes can be identified. One is hydration water around proteins. The second is a glass forming process of unknown origin. The paper will discuss its possible origin and if it could be linked to anti-freeze properties in the flesh of fish.

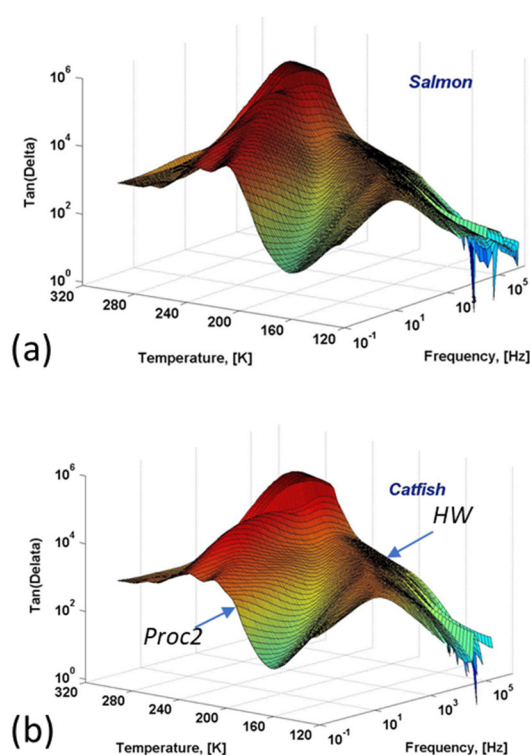


Figure 1 The loss tangent for (a) Salmon and (b) catfish. The measurements were made in the temperature range $-100\text{ }^{\circ}\text{C}$ to $12\text{ }^{\circ}\text{C}$ and frequency range 10^{-1} Hz to 100 kHz . The main processes are highlighted in (b). 'HW' refers to hydration water around an antifreeze protein.

Keywords— Dielectric Spectroscopy, water, frozen food, interfacial water

Resolving a Mystery of the Molecular Dynamics of Epoxy-based Materials Using Broadband Dielectric Spectroscopy and Hyphenated Calorimetry

Paulina Szymoniak, Hassan Omar, Xintong Qu, Andreas Schönhals

Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

Although in the last decades epoxy-based nanocomposites have been successfully adopted by the marine, automotive and aerospace industries they are still rarely studied on a fundamental level. This work deals with an in-depth comparative investigation of the structure, molecular mobility and vitrification kinetics of three bisphenol A diglycidyl ether (DGEBA)-based materials with different nanofillers: *I*) taurine-modified layered double hydroxide (T-LDH), *II*) boehmite (BNPs) and *III*) halloysite nanotubes (HNTs). Moreover, the effect of different hardeners (diethylene triamine and methyl tetrahydrophthalic acid anhydride) on the unfilled epoxy matrix is addressed as well. The chosen methodology comprises *I*) small – and wide – angle X-ray scattering (SAXS/WAXS) *II*) calorimetry in the forms of *a*) conventional DSC and *b*) static fast scanning calorimetry (FSC), *III*) broadband dielectric spectroscopy (BDS), as well as *IV*) specific heat spectroscopy in the forms of *a*) temperature modulated DSC, and *b*) temperature modulated FSC. The combination of these techniques proved an intrinsic spatial heterogeneity of epoxy-based materials, evidenced by two separate segmental relaxation processes. Although, depending on the hardener the response of the systems to calorimetric and dielectric investigations was different, in a broader sense similar conclusions can be extracted on the structural heterogeneity. As expected from the two distinct α -processes, it was shown that, in parallel to the main glass transition, epoxy-based materials can exhibit an additional low temperature vitrification mechanism, which was not discussed in prior studies for an unfilled network former. Furthermore, the interfacial region (so-called rigid amorphous fraction) was qualitatively and quantitatively addressed, in dependence of the employed nanofiller structure.

Transient Dynamics of Cold-Rolled Atactic-Polystyrene Using Broadband Dielectric Spectroscopy.

Michael Wübbenhorst

Department of Physics and Astronomy, KU Leuven, Leuven, Belgium

The effect of plastic deformation on the molecular dynamics of atactic polystyrene (a-PS) was studied by broadband dielectric relaxation spectroscopy (BDRS), Fourier-transform infrared spectroscopy (FTIR) and above its glass-transition temperature, resulting in thermal rejuvenation. Cold rolling revealed, in addition to the known α - and γ (I)-relaxations, four hitherto unknown relaxation processes (II, III, IV and V). Using the framework of craze formation and multiplicity of the glass transition, supported by an activation-enthalpy/entropy analysis, the following physical picture emerges: i) Processes I and II represent local conformation transitions referring to chains of two different degrees of stretching (T/G-ratio); ii) processes III and IV were identified as helix-inversion processes of T₂G₂ helices as reported earlier for syndiotactic-rich PS - an assignment supported by FTIR results. Finally, the relaxation V could be attributed to the onset of the fibrillar glass transition (within crazes), leading to stress release by collapse of the fibrils and hence dying out of process V. Polarized-light microscopy confirmed the creation of oriented structures and internal stresses upon cold rolling, and their removal upon thermal rejuvenation.

Nonequilibrium dynamics of interfacial polymer layers

C Rodríguez-Tinoco, Z, Song, A Mathew and S S Napolitano

*Laboratory of Polymer and Soft Matter Dynamics,
Experimental Soft Matter and Thermal Physics (EST),
Faculté des Sciences, Université libre de Bruxelles (ULB),
Boulevard du Triomphe, Brussels 1050, Belgium*

We show that adequately processing thin films of poly(4-chlorostyrene) under nonequilibrium conditions induces an enhancement in segmental mobility. This procedure is achieved by spincoating the polymer layer on rough aluminum substrates [1]. Faster dynamics is observed on rougher substrates.

This trend is in contrast to existing treatments of roughness based on equilibrium arguments which conclude it is a source of slower dynamics. Our experimental evidence indicates that faster interfacial dynamics originate from a reduction in interfacial density, due to the noncomplete filling of substrate asperities. The nonequilibrium component of this confinement effect is associated to a long-living metastable state, stable up to timescales almost one billion times larger than the segmental relaxation time.

Importantly, our results agree with the same scaling that describes the density dependence of bulk materials, correlating segmental mobility to a term exponential in the specific volume, and with empirical relations linking an increase in glass transition temperature to larger interfacial energy.

Remarkably, experiments on rough silicon substrates show the trend predicted by theory in systems at thermodynamic equilibrium [2]. Based on this observation, we anticipate the existence of a faster equilibration pathway active on silicon.

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[2] A Beena Unni, al, R Richert and K Adrjanowicz Experimental evidence on the effect of substrate roughness on segmental dynamics of confined polymer films Polymer, 199, 122501 (2020)

Polymers under 2-D confinement: In situ polymer imbibition in nanopores

Chien-Hua Tu,¹ George Floudas^{1,2}

¹ *Max Planck Institute for Polymer Research, 55128 Mainz, Germany*

² *Department of Physics, University of Ioannina, 45110 Ioannina, Greece*

Abstract

Understanding that way that polymers penetrate in narrow pores is important for applications including separation of proteins with relevance in cell biology and the development of inkjet printing for commercial xerography. Placing macromolecules close to interfaces alter their conformational and dynamic properties. Much of this behavior stems from polymer-substrate interactions.¹ A recent advancement in this field have been experiments by the so-called, *nanodielectric* method.² The method offers simultaneous access to the kinetics of imbibition and to the molecular dynamics during flow at the segmental and chain length scales. Results have demonstrated the potential of the method to extract *quantitative* information on the viscosity experienced by the polymer during flow.³ Here we employ *in-situ* nanodielectric spectroscopy to demonstrate that the imbibition kinetics of *cis*-1,4-polyisoprene in native alumina nanopores proceeds in two time-regimes both with higher effective viscosity than bulk. This finding is discussed by a microscopic picture that considers the competition from an increasing number of chains entering the pores and a decreasing number of fluctuating chain-ends. The latter is a direct manifestation of increasing adsorption sites during flow.⁴

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The segmental dynamics of polymer films confined on a substrate

Aparna Beena Unni,^{1,2} Katarzyna Chat,^{1,2} Katarzyna Balin,^{1,2} Daniel Marques Duarte,^{1,2} Marcin Wojtyniak,^{1,2} Monika Geppert-Rybczyńska,³ Jerzy Kubacki,¹ Roman Wrzalik,^{1,2} Ranko Richert⁴ and Karolina Adrjanowicz^{1,2}

¹ *Institute of Physics, University of Silesia, 75 Pulku Piechoty 1, 41-500 Chorzow, Poland*

² *Silesian Center for Education and Interdisciplinary Research (SMCEBI), 75 Pulku Piechoty 1a, 41-500 Chorzow, Poland*

³ *Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland*

⁴ *School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA*

Polymers show a lot of anomalous behavior when they are confined by the thickness. When the thickness is reduced, we found an increase in the dynamics of poly-(4-chlorostyrene) on silicon substrate until it reaches the thickness of around 10 nm; at the 10 nm the film exhibits bulk like behaviour.[1] We try to explain the deviations in the segmental dynamics in confined polymer films based on their density distribution obtained by Time-of-Flight Secondary Ion Mass Spectrometry.

Another point to address is, even the nanometric variations in the surface roughness can significantly influence the dynamics of confined polymer films. The polymer was spin coated onto silicon substrates with different values of surface roughness controlled by plasma treatment. We have observed a slowing down of segmental mobility with increasing roughness using broadband dielectric spectroscopy.[2] It was also possible to recover bulk like behaviour in confined polymer films by tuning substrate roughness.

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

S. Soreto Teixeira¹, N. Gama², T. Cordeiro³, M. P. F. Graça¹, A. Barros-Timmons², M. Dionísio³, L. C. Costa¹

1- *I3N and Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal*

2- *CICECO and Department of Chemistry, University of Aveiro
3810-193 Aveiro, Portugal;*

3- *REQUIMTE, Department of Chemistry, Faculdade de Ciências e Tecnologia da
Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

Lithium ferrite, LiFe_5O_8 (LFO), is an interesting material for several technological applications, due to its particular electrical and magnetic properties. This work aims to study the physical properties of a composite, obtained by LFO particles embedded in a polymer matrix, PLLA. LFO powders were obtained by solid state reaction and then heat treated at 1100 °C, which is the temperature at which it is mainly in the crystalline phase. The composites were prepared by dispersing LFO in concentrations ranging from 0 to 20 % (wt/wt) in the biopolymer poly(L-lactic acid) (PLLA). The ensuing composites were characterized by X-ray diffraction, thermal analysis and impedance spectroscopy (IS). The IS measurements were performed between 10^{-1} and 10^6 Hz, covering a temperature range from -120 to 140 °C. A correlation was found between electrical properties and LFO particles concentration. For the low LFO concentration composites (< 5% wt), three relaxations were detected, as found for the neat PLLA: a dominant α process, associated with the dynamic glass transition, and two secondary processes; the one located in the high frequency regime has the characteristic features of a Johari-Goldstein (JG) relaxation taken as the precursor of the α relaxation. The latter broadens as the LFO concentration increases although its temperature location does not undergo significant changes relative to neat PLLA. For the high LFO content composites, the dielectric properties are dominated by the conductivity. The temperature dependence of the detected relaxation processes and conductivity were analysed, allowing the construction of a relaxation map, which provides the dynamic fingerprint of the material.

Universal correlation between the electromagnetic interference shielding effectiveness of composite materials and their spectroscopic electrical impedance.

Anatoli Serghei

Université Claude Bernard Lyon 1, INSA de Lyon, Ingénierie des Matériaux Polymères (UMR CNRS 5223), 15 Boulevard Latarjet, Villeurbanne Cedex 69622, France

With the tremendous technological developments related to the accelerated growth in the field of telecommunications, our contemporary society is increasingly facing the problem of electromagnetic pollution. The electromagnetic pollution, expected to grow even faster in the coming years, leads to electromagnetic interference phenomena that disturb the correct functioning of instruments and systems, posing thereby an important risk to industrial applications and human being. Developing technological solutions and materials for protecting people, instruments and systems from electromagnetic interference phenomena becomes thus a major challenge in our society.

In the current study, the electromagnetic interference shielding properties and the electrical properties of different types of materials, such as polymethylmethacrylate (PMMA) based composite materials prepared using different types of fillers (multiwall carbon nanotubes, carbon black, silver coated glass microfibers), metalized layers, metallic wires have been investigated. To this purpose, two broadband experimental methods have been employed: coaxial cell method for measuring the shielding effectiveness between 50 kHz and 1 GHz and Broadband Dielectric Spectroscopy to characterize the electrical properties between 1 Hz and 10 MHz. By combining a theoretical and an experimental analysis we show that, irrespective of the nature of the conductive material (carbon based or metallic), the correlation between the electromagnetic shielding performance at low frequencies and the electrical impedance follows a universal behavior, all experimental points falling onto a single universal curve. This is demonstrated not only for our own experimental results, but also for experimental data reported in the literature where other types of polymer matrices and other types of fillers have been investigated. Furthermore, for materials exhibiting both a resistive and a reactive electrical contribution, our analysis demonstrates, for the first time, a complete inter-conversion between the frequency dependence of the shielding effectiveness and the frequency dependence of the electrical impedance. These findings open the perspective of a predictive design of electromagnetic shielding materials based exclusively on their electrical properties.

Physical vapor deposition onto interdigitated electrode cells

Erik Thoms, Jan P. Gabriel, Ranko Richert

School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA

Interdigitated electrode (IDE) cells, see Fig. 1, are useful for a variety of dielectric and conductivity studies where a parallel plate geometry is not feasible [1]. This is particularly true for dielectric relaxation experiments on samples prepared by physical vapor deposition. As indicated in the cross-sectional schematic of Fig. 2, the substrate, often borosilicate glass, also contributes to the signal, and a careful subtraction of ϵ_{sub} is required, especially for thin or nonpolar films. This can be achieved by measuring the empty cell separately, or by simultaneously measuring both IDE structures in a differential cell as in Fig. 1, making sure only one side is exposed to vapor deposition [2,3].

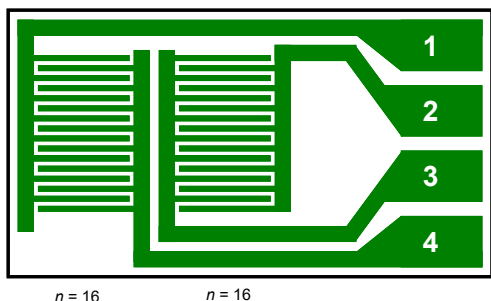
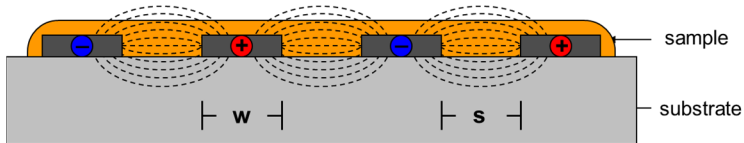


FIG. 1



$$\epsilon = \frac{C}{C_{\text{geo}}} = \frac{h(\epsilon_{\text{sam}} - 1) + 1}{2} + \frac{\epsilon_{\text{sub}}}{2}$$

FIG. 2

Because the field is not homogenous (dashed lines in Fig. 2), it is not trivial to obtain reliable values for the permittivity of a film of arbitrary thickness. For the average field height, one can find both $(w + s)$ and $(w + s)/4$ as answers, where w is the digit width and s the digit spacing, see Fig. 2. Interestingly, both are valid answers, depending on the situation.

Using resolutions regarding capacitance and $\tan \delta$ of about 50 aF and $< 10^{-6}$, respectively, film growth can be monitored with a resolution of a fraction of a nanometer, and the existence of a mobile surface layer during the deposition of a kinetically stable glass can be observed by dielectric techniques.

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Lateral resolution and spectral bandwidth of local dielectric spectroscopy

M. Labardi¹, R. Casalini², S. Capaccioli^{1,3}

¹ *CNR-IPCF, Sede Secondaria di Pisa (Italy)*

² *Chemistry Division, Naval Research Laboratory, Washington DC (USA)*

³ *Physics Department, University of Pisa (Italy)*

Abstract. Local Dielectric Spectroscopy (LDS) [1], based on Atomic Force Microscopy (AFM), is emerging as a unique tool for the investigation of dielectric relaxation dynamics resolved in real space with nanometer scale resolution. While state of the art performance provides a frequency range of about 5 decades and a spatial resolution of 20-30 nm, recent efforts have been devoted in our group to the improvement of both spectral range and spatial resolution of LDS [2,3]. Wider spectral bandwidth is desirable to follow the dynamics over a broader range of relaxation times and better resolve the shape of the relaxation functions. On the other hand, increasing the resolving power down to a few nanometers would give access to a number of characteristic length scales of physical interest, like for instance the dynamic correlation length in glass-forming systems or the mobility gradient for polymers close to nano-interfaces. In this seminar, the operation principle of Broadband Local Dielectric Spectroscopy (BLDS) [2] is recalled, and some experimental results on polymeric nanocomposites reviewed. Recent results on spatial resolution improvement of local dielectric measurements down to 2-3 nm will be also shown [3], obtained by exploiting a peculiar operation mode of AFM named constant-excitation frequency-modulation (CE-FM) mode, that facilitates operation in ambient conditions [4]. These results are a promising step towards application to LDS, to achieve the same degree of local resolution also in spectroscopic measurements.

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Desorption dynamics in polymer nanocomposites through a combination of dielectric spectroscopy and rheology

Shiwang Cheng

*College of Engineering, Michigan State University,
Engineering Building, 428 S. Shaw Lane, East Lansing, MI 48824*

Polymer adsorbed onto the surface of nanoparticles forming bound polymer layer, which is known to play a crucial role in the advanced mechanical properties of polymer nanocomposites (PNCs). Due to the complex geometry of the PNCs, the dynamics of the bound polymer remain largely unknown. In this contribution, we show the basic characteristics of the dynamics of the bound polymer through dielectric normal mode analyses. Moreover, a combination of the dielectric and rheology enables unraveling the characteristics of the dynamics of polymer desorption that cannot be easily access otherwise. These results clearly demonstrate the unique capability of the dielectric spectroscopy as a selective tool to quantify the slow dynamics of PNCs.

Generic structural relaxation in molecular liquids: Photon correlation and NMR spectroscopy vs dielectric spectroscopy

T. Körber,¹ R. Stäglich,¹ C. Gainaru², R. Böhmer², E. A. Rössler¹

¹ *Anorganische Chemie III and Nordbayerisches NMR Zentrum, Universität Bayreuth,
95440 Bayreuth, Germany*

² *Fakultät Physik, Technische Universität Dortmund, 44221 Dortmund, Germany*

Relaxation spectra of molecular glass formers devoid of secondary relaxation maxima, as measured by dielectric spectroscopy (DS), nuclear magnetic resonance (NMR) relaxometry, photon correlation spectroscopy (PCS), and Fabry-Perot interferometry are quantitatively compared in terms of the Kohlrausch stretching parameter β_K close to T_g . For a reliable estimate of β_K the excess wing contribution was included in the spectral analysis, i.e., in type A liquids the parameterization of the α relaxation, without taking into account the presence of an excess wing, is prone to being unreliable. The relaxation stretching probed by PCS and NMR varies only weakly among the liquids ($\beta_K = 0.58 \pm 0.06$). It is similar to that found in DS, provided that the liquid is sufficiently nonpolar (relaxation strength $\Delta\epsilon \lesssim 6$). For larger strengths, larger β_K^{DS} (narrowed relaxation spectra) are found when compared to those reported from NMR and PCS. In other words, we suggest a generic relaxation stretching in molecular liquids.¹

Frequency-temperature superposition (FTS) holds for PCS and NMR. This is demonstrated by data scaling and, for the few glass formers for which results are available, by the equivalence of the susceptibilities $\chi''_{PCS}(\omega\tau) \propto \chi''_{NMR}(\tau) \propto \chi''_{NMR}(\omega)$, i.e., measuring at constant frequency is equivalent to measuring at constant temperature or constant correlation time. In this context, a plot of the spin-lattice relaxation rate $R_1(T)$ as a function of the spin-spin relaxation rate $R_2(T)$ is suggested to reveal the stretching parameter without the need to perform frequency-dependent investigations. Dielectrically, we identify a trend of increasing deviations from FTS with increasing $\Delta\epsilon$. Depending on technique and glass former, the relative relaxation strength of the excess wing varies, whereas its exponent appears to be method independent for a given substance.

As recently shown by Blochowicz and coworkers,^{2,3} it is likely that cross-relaxation effects are responsible for the joint occurrence of relatively high dielectric strengths and narrow spectral widths – and not a contribution from the dipole-dipole interaction to the attractive part of the intermolecular potential as suggested by Paluch et al..⁴ In an attempt to quantify the system-specific cross-relaxation effects in polar liquids, however, we could not confirm the notion that these are related to the Kirkwood factor.

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Correlating microscopic heterogeneity and dynamics in deep eutectic solvents

Stephanie Spittle¹, Derrick Poe², Charles Kolodziej³, Yong Zhang², Clemens Burda³, Thomas Zawodzinski¹, Edward J. Maginn², and Joshua Sangoro^{1*}

¹*Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN*

²*Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN*

³*Department of Chemistry, Case Western Reserve University, Cleveland, OH*

*jsangoro@utk.edu

Non-aqueous solvents that are scalable, easy to prepare and functionalize are needed in many applications ranging from biomass processing to energy storage technologies. Deep eutectic solvents (DESs) present a large design space and are highly tunable for specific applications. To correlate local structure to macroscopic dynamics, we carried out a detailed study on model DESs including Glyceline and Ethaline by employing broadband dielectric spectroscopy complemented by a range of computational and experimental techniques that span length-scales from molecular to macroscopic and timescales from picoseconds to seconds. We find that the microscopic heterogeneities induced in hydrogen bond donors by the addition of the hydrogen bond acceptors such as choline chloride lead to new slow, relaxation modes that are strongly correlated to the macroscopic properties of the DES formed. These results provide a unified framework for rationalizing the key features of choline based DESs including a decreased glass transition temperature and a corresponding increase in dc ionic conductivity, fluidity, diffusivity, and the mean rates of orientational molecular dynamics.

Universal Structural Relaxation in Supercooled Liquids and the Role of Cross-correlations in Dielectric Spectroscopy

Florian Pabst,¹ Jan Gabriel,² Till Böhmer,¹ Peter Weigl,¹ Andreas Helbling,¹ Timo Richter,¹ Parvaneh Zourchang,¹ Thomas Walther,³ and Thomas Blochowicz¹

¹ *Institute of Condensed Matter Physics, Technical University of Darmstadt, 64289 Darmstadt, Germany.*

² *School of Molecular Sciences, Arizona State University, Tempe, AZ 85287-1604, USA.*

³ *Institute of Applied Physics, Technical University of Darmstadt, 64289 Darmstadt, Germany.*

One of the hallmarks of molecular dynamics in deeply supercooled liquids is the non-exponential character of the relaxation functions. It has been a long standing issue if „universal“ features govern the lineshape of glassy dynamics independent of any particular molecular structure or interaction or if there is some kind of „generic“ α -relaxation, maybe only observed in very few particularly simple liquids. In the present work we elucidate this problem by giving a detailed comparison of the spectral shape of depolarized light scattering and dielectric data of deeply supercooled liquids. It turns out that the light scattering spectra of very different systems, like hydrogen bonding and van der Waals liquids but also ionic systems almost perfectly superimpose and show a generic lineshape of the structural relaxation, approximately characterized by a high frequency power law $\omega^{-1/2}$. The dielectric loss peak, on the other hand, apparently shows a much narrower and more individual shape. An explanation starts from the observation of the so-called Debye process which is well known in the dielectric spectra of monohydroxy alcohols but from recent theoretical considerations is expected to appear more generally in the dielectric loss of dipolar liquids as soon as cross-correlations due to dipole-dipole or other interactions become important. And indeed, an analysis of dielectric and light scattering data is able to distinguish cross-correlation contributions in several strongly dipolar systems, while in the low dipolar silicon oil DC704, which is considered as a simple liquid in the literature, the shape of dielectric loss and light scattering susceptibility becomes identical due to lack of cross-correlations.

Thus, a generic lineshape is indeed confirmed in the dynamics of deeply supercooled liquids. In the dielectric loss the latter is simply covered by strong cross-correlation contributions, which dominate the dielectric spectra in strongly dipolar systems.