## **BOOK OF ABSTRACTS**

## **INERA Workshop**

# Membrane and Liquid Crystal Nanostructures

(MELINA)

September 4 – 5, 2016

Varna, Bulgaria

The INERA WORKSHOP MELINA is organized in the framework of the FP7 Project REGPOT 316309 by the Institute of Solid State Physics, Bulgarian Academy of Sciences

## **Topics:**

- 1. Nanostructured liquid crystal systems and nanocomposites
- 2. Soft and living matter physics
- 3. Membrane biophysics
- 4. Nanostructures in polymer and lipid membranes
- 5. Characterization of soft nanomaterials

## Scientific sessions:

- 1. Membrane biophysics
- 2. Soft and living matter physics
- 3. Nanocomposites and polymers

Chairman: Academician Alexander G. Petrov Vice-Chairman: Professor Kiril Blagoev Scientific Secretary: Professor Minko Petrov

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# **PROGRAMME**

## SUNDAY, 4<sup>TH</sup> SEPTEMBER, 2016

#### 9:00 – 9:10 **OPENING**

Academician Alexander G. Petrov, MELINA Chairman, INERA Project Coordinator

## SESSION 1: MEMBRANE BIOPHYSICS

### Part I. Chair: Alexander G. Petrov

## 9:10 – 9:50 <u>Thomas Rainer Heimburg</u> Mechano-capacitive properties of polarized membranes 9:50 – 10:30 <u>Margarita Staykova</u> Membranes on deformable substrates - biological insights and technological applications 10:30 – 10:50 <u>Ksenia Chekashkina</u>, P.I. Kuzmin, V.A. Frolov, P.V. Bashkirov The regulation of membrane bending rigidity by components with high intrinsic curvature

#### **10:50 – 11:20 COFFEE BREAK**

## Part II. Chair: Isak Bivas

11:20 – 12:00 <u>Aleš Iglič</u>, L. Mesarec, M. Fošnarič, S. Penič, S. Kralj, W. Góźdź, V. Kralj-Iglič

On the mechanisms of membrane tubulation

12:00 – 12:20 <u>Yury Ermakov</u>

Boundary potential of lipid bilayers: methods and interpretations

12:20 – 12:40Anna Gavrilchik, V.S. SokolovInvestigation of the photodynamic processes on the surface of<br/>bilayer lipid membrane by method of intramembrane field<br/>compensation (IFC)

#### 13:00 – 14:00 LUNCH

## SUNDAY, 4<sup>TH</sup> SEPTEMBER, 2016

## **SESSION 1: MEMBRANE BIOPHYSICS**

### Part III. Chair: Thomas Heimburg

14:00 – 14:40 <u>Galya Staneva</u>, R. Georgieva, Kr. Mircheva, V. Vitkova, K. Balashev, T. Ivanova, C. Tessier, K. Koumanov, P. Nuss, A. Momchilova,

*Phospholipase* A<sub>2</sub> *induced remodeling processes on liquidordered/liquid-disordered bilayers mimicking cellular plasma membranes* 

14:40 – 15:00Oleg Batishchev, E.V. Shtykova, L.A. Shilova, L.A. Baratova,<br/>N.V. Fedorova, T.R. Galimzyanov

Structural analysis of self-assembly of Influenza A virus protein scaffold

- 15:00 15:20Sergey Akimov, V.V. Aleskandrova, T.R. GalimzyanovMechanism of lipidic pore formation by antimicrobial peptides
- **15:20 15:50 COFFEE BREAK**

## SESSION 2: SOFT AND LIVING MATTER PHYSICS

## Chair: Victoria Vitkova

15:50 - 16:30	<u>Alexander G. Petrov</u>		
	Bioflexoelectricity and biohelielectricity		
16:30 - 16:50	Isak Bivas, Nikolay Tonchev		
	Statistical Mechanics of Fluctuating Vesicle		
16:50 - 17:10	Hassan Chamati, R. Trobec, J. I. Pavlič		
	Structural Properties of Pre-formed DPPC and DSPC Lipid Vesicles: A Coarse Grain Molecular Dynamics		
17:30 - 18:30	POSTER SESSION		

20:00 – 21:00 DINNER

## MONDAY, 5<sup>TH</sup> SEPTEMBER, 2016

## SESSION 3: NANOCOMPOSITES AND POLYMERS

## Part I. Chair: Minko Petrov

- 9:30 10:10 <u>Paul Montgomery</u> Optical nanoscopy characterization of nanofilms
- 10:10 10:50Oliver WilliamsS. Mandal, E.L.H. Thomas, G. Klemencic,<br/>L. Gines, J. Werrell, S. Giblin<br/>Nanostructured diamond for Quantum applications
- **10:50 11:20 COFFEE BREAK**

## Part II. Chair: Nikolay Tonchev

- 11:20 12:00Michele Giocondo,<br/>T. Ritacco, L. Ricciardi, M. La DedaAdditive Manufacturing of metallic nanoparticles structures by<br/>2-photons Direct Laser Writing
- 12:00 12:40Marcus Cook,<br/>Marcus Cook,<br/>L. Peeva, D. Mitev, E. Radeva, A. Livingston<br/>Chemical Vapour Deposition for the fabrication/modification of<br/>nanofiltration membranes
- 12:40 13:00Kostadinka Gesheva, T. Ivanova, S. Boyadjiev<br/>Chromogenic Smart Nanocomposites as Functional Surfaces in<br/>Energy Efficient Devices
- 13:00 14:00 LUNCH

## MONDAY, 5<sup>TH</sup> SEPTEMBER, 2016

## SESSION 3: NANOCOMPOSITES AND POLYMERS

## Part III. Chair: Galya Staneva

- 14:00 14:40Samo Kralj, P. Kuryoz, S. RzoskaSupercooled Soft Nanocomposites
- 14:40 15:00N. Hristova-Avakumova, B. Nikolova-Mladenova, K. Yoncheva,<br/>Vera Hadjimitova,

Novel Hydrazones – Antioxidant Potential and Stabilization via Polysaccharide Particle

- **15:00 15:20Dimiter Mitev**, D. Peshev, G. Peev, L. PeevaDepot effect of bioactive components in experimental membrane<br/>filtrations
- 15:20 15:40 CLOSING

#### 20:00 – 23:00 FAREWELL PARTY

## **POSTER SESSION**

## SUNDAY, 4<sup>TH</sup> SEPTEMBER, 2016, 17:30-18:30 h

P-1 Hari Krishna Koduru, M. Iliev, Y. Marinov, D. Karashanova, N. Scaramuzza:

Synergetic effect of  $TiO_2$  nanofillers and  $NaIO_4$  additives on conductivity and dielectric properties of PEO/PVP nanocomposite electrolytes for electrochemical cell applications

P – 2 <u>Hari Krishna Koduru</u>:

Electro-optical and dielectric characterization of nano-PDLC films

P-3 <u>Ch. Angelov</u>:

Advanced atmospheric investigations at basic environmental observatory "Moussala"

**P**-4 <u>G. B. Hadjichristov</u>, Y. G. Marinov:

*Photoresponsive azo-doped Aerosil/7CB nematic liquid-crystalline nanocomposite films: the role of polyimide alignment layers of the films* 

- P-5 <u>K. Antonova</u>, C. Meyer, I. Dozov:
   Double helices in chiral smectics under electric field
- **P-6** <u>A. Vasev</u>, M. Iliev, A. Stoyanova-Ivanova, V. Mikli, M. Marinov, Y. Marinov:

Electrochemical impedance spectroscopy of YBCO ceramics

- P 7 <u>Y. G. Marinov</u>, M. P. Marinov, G. B. Hadjichristov, S. K. Prasad, L. Marino, N. Scaramuzza:
   *Dielectric study of azo-doped aerosil/7CB filled nematic upon UV light*
- P-8 <u>V. Vitkova</u>, G. Coupier, T. Podgorski:
   *Rheological properties of erythrocyte suspensions*
- P-9 <u>D. Mitkova</u>, K. Antonova, R. Dimova, V. Vitkova:
   Sugar effect on lipid membranes measured by flicker spectroscopy, electrodeformation and electroporation of lipid vesicles
- **P 10** K. Zhelyazkova, M. Petrov, B. Katranchev, H. Naradikian, <u>G. Dyankov:</u>

Surface plasmon for exploration the temperature dependence of hybrid cholesteric liquid crystal's pitch

E. Zachanowicz, A. Zięcina, M. Małecka, K. Marycz, M. Marędziak, B.
 Poźniak, M. Nowakowska, M. Tikhomirov, J. Miller, R.J. Wiglusz, R. Pązik, K. Rogacki:

Cytotoxic effects of  $Co_{1-x}Mn_xFe_2O_4$  ferrite nanoparticles synthesized under non-hydrolytic conditions (Bradley's reaction) - in vitro

P-12 <u>H. Naradikian</u>, M. Petrov, B. Katranchev, T. Milenov, S. Tinchev:

Surface characterization and orientation interaction between diamond-like carbon layer structure and dimeric liquid crystals

P-13 <u>G. Exner</u>, Y. G. Marinov, E. Perez:

Investigation of the structure and thermal behaviour of polymer liquid crystal/single wall carbon nanotubes nanocomposites

P-14 M. Petrov, B. Katranchev, P. Rafailov:

The unique physical properties of the hydrogen bonded in dimers liquid crystals

 P-15 <u>S. Boyadjiev</u>, B. Manduca, O. Kéri, P. Bárdos, K. A. Gesheva, I. M. Szilágyi: *Transition metal oxides core-shell nanocomposites prepared by combination of various techniques with atomic layer deposition for photocatalytic, electrochromic and gas sensing applications*

# INVITED LECTURES

### Mechano-capacitive properties of polarized membranes

#### L. D. Mosgaard, K. Zecchi, T. Heimburg\*

#### Niels Bohr Institute, University of Copenhagen, Denmark \* <u>theimbu@nbi.ku.dk</u>

Biological membranes are capacitors that can be charged by applying a field across the membrane. The charges on the capacitor exert a force on the membrane that leads to electrostriction, i.e. a thinning of the membrane. Since the force is quadratic in voltage, negative and positive voltages have an identical influence on the physics of symmetric membranes.

However, this is not the case for a membrane with an asymmetry leading to a permanent electric polarization. Positive and negative voltages of identical magnitude lead to different properties. Such an asymmetry can originate from a lipid composition that is different on the two monolayers of the membrane, or from membrane curvature. The latter effect is called 'flexoelectricity'. As a consequence of permanent polarization, the membrane capacitor is discharged at a voltage different from zero. This leads to interesting electrical phenomena such as outward or inward rectification of membrane permeability.

Here, we introduce a generalized theoretical framework that treats capacitance, polarization, flexoelectricity, piezoelectricity and thermoelectricity in the same language. We show applications to electrostriction, membrane permeability and piezoelectricity and thermoelectricity close to melting transitions, where such effects are especially pronounced. These findings are particularly interesting in the context of nerve pulse propagation.

#### **Optical nanoscopy characterization of nanofilms**

P.C. Montgomery<sup>1,\*</sup>, P. Chapuis<sup>2,3</sup>, F. Anstotz<sup>1</sup>, A. Leong-Hoi<sup>1</sup>, A. Rubin<sup>2</sup>, J. Baschnagel<sup>2</sup>, C. Gauthier<sup>2</sup>, G. Reiter<sup>3</sup>, G.B. McKenna<sup>4</sup>

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 <sup>2</sup> Institut Charles Sadron (ICS), 23 rue du Loess, Strasbourg, France.
 <sup>3</sup> Inst. of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany.
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Glass formation and glassy behavior remains an important field of study in condensed matter physics, with many aspects still little understood. One approach is to observe the changes in behavior of glass-forming materials at the nanometer scale. In this work, the viscoelastic properties of ultrathin free-standing glassy polymer films are explored using an experimental measurement cell based on the nanobubble inflation method [1]. This consists of inflating a polymer film suspended over an array of 5  $\mu$ m diameter holes in a Si wafer held in the cell. Measuring the deformation as a function of time as the material relaxes is used to determine the creep compliance.

Both polystyrene (PS) and poly(vinyl acetate) (PVAc) films of a few tens of nm thickness have been prepared by spin-coating from solution in toluene onto a Si wafer and manually transferring the film onto the perforated substrate using a water bath. Interference microscopy, more commonly used for surface roughness measurement [2], is used to measure the change in deformation over several hours. The advantages of this technique compared with AFM are that it is non-contacting, provides a much wider field of view and has a faster acquisition time ( $\sim 5$  s instead of  $\sim 10$  min for AFM). Although the axial sensitivity of interference microscopy can be better than 1 nm, achieving high accuracy can be a challenge [3]. Nanoscale measurements of a surface deforming over several hours presents further difficulties due to mechanical deformations and drift. In this paper we present some of the first solutions developed to allow consistent measurements of film deformation using this novel interference as a function of different film properties and the results will be compared with theoretical predictions.

<sup>[1]</sup> P.A. O'Connell and G. B. McKenna, Rheological measurements of the thermoviscoelastic response of ultrathin polymer films, *Science* **307** (2005) 1760-1763.

<sup>[2]</sup> P.De Groot, Principles of interference microscopy for the measurement of surface topography, *Advances in Optics and Photonics* 7 (2015) 1–65.

<sup>[3]</sup> P.C. Montgomery, M. Guellil, P. Pfeiffer, B. Serio and L. Pramatarova., Challenges in the areal measurement of surface roughness and shape at the micro and nanoscale, *Journal of Physics Conference Series* 558 (2014) 012005.

#### Adaptation of lipid membranes to surface area changes

Margarita Staykova

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The physical coat of biological cells is remarkable in its ability to adapt and respond to mechanical stretch. For example, the cell residents of hollow organs, such as lungs, bladder, kidney, etc. can change their surface area with up to 80%. However, the molecular mechanisms of such mechanical adaptation remain unclear.

We approach this question by taking into account the mechanical architecture of the cell interface- a plasma lipid membrane underlined by an actin cortex. Whereas the cortex is elastic and actively reshaping structure, the lipid membrane can withstand only 2-3% stretch before rupture [1]. To understand this apparent contradiction we have coupled a lipid bilayer to a deformable substrate and have imaged the membrane response upon substrate area changes of controlled rate and amplitude [2]. We show that the membrane can follow the expansion of the substrate by absorbing folds or infused vesicles adhered to it; upon compression, lipid protrusions grow out of the membrane plane, thus reducing its area [3]. Our suggestion of similar mechanisms operating in biological membranes has been recently confirmed by experiments on cells attached to elastic substrates [4]. Moreover, in our latest work [5], we show that depending on the coupling to the substrate, membranes can also accommodate area changes by sliding over the expanding/shrinking substrate.

Creating artificial systems that capture the elasticity and deformability of the cell interface can provide invaluable insights into the mechanisms of mechano-transduction in cells, and the principles conferring biological membranes with the ability to dynamically remodel and to sustain mechanical stresses. We further expect that such systems will open new horizons for the current lipid technologies, including flexible biosensors and lipogel capsules that can reversibly change their shape, adhesivity and permeability in response to chemical and mechanical stimuli.

- [1] D. Needham and R. S. Nunn, *Biophys. J.* 58 (1990) 997–1009.
- [2] M. Staykova, D. P. Holmes, C. Read and H. A. Stone, Proc. Natl. Acad. Sci. U. S. A. 108 (2011) 9084–9088.
- [3] M. Staykova, M. Arroyo, M. Rahimi and H. A. Stone, Phys. Rev. Lett. 110 (2013) 1–5.
- [4] A. J. Kosmalska et al., *Nature Commun.* 6 (2015) 7292.
- [5] L. Stubbington, M. Arroyo and M. Staykova, Soft Matter (2016). doi:10.1039/C6SM00786D

#### On the mechanisms of membrane tubulation

<u>A. Iglič</u><sup>1,\*</sup>, L. Mesarec<sup>1</sup>, M. Fošnarič<sup>1</sup>, S. Penič<sup>1</sup>, S. Kralj<sup>2</sup>, W. Góźdź<sup>3</sup>, V. Kralj-Iglič

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 <sup>3</sup>Polish Academy of Science, Warsaw, Poland
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We present a physical mechanism that may explain experimentally observed tubular and spherical budding of biological membrane. The proposed mechanism is based on the energetically favourable self-assembly of membrane nanodomains into larger membrane domains forming spherical, tubular or undulated tubular membrane protrusions (see Figure 1). The proposed mechanism of growth and stabilization of membrane protrusions by coupling of the local membrane shape and the lateral density of the membrane constituents (nanodomains) is also one of the mechanisms relevant for the formation and stabilization of tunneling nanotubes that connect cells, and could be important in intracellular and intercellular transport and communication.



**Figure 1**. Monte Carlo simulations of the 3-D shape of closed vesicle. The membrane of the vesicles is composed of two components having zero (blue colour) and positive intrinsic curvature (red colour), respectively. The phase segregation and the formation of long undulated tubular protrusion are observed at large concentration of membrane components/nanodomains with positive intrinsic (spontaneous) curvature. The direct interactions between nanodomains are taken into account.

- L. Mesarec, W. Góźdź, V. Kralj Iglič, S. Kralj and A. Iglič, Closed membrane shapes with attached BAR domains subject to external force of actin filaments, *Colloids and Surfaces B: Biointerfaces* 141: (2016) 132–140.
- [2] N. Bobrovska, W. Góźdź, V. Kralj-Iglič and A. Iglič: On the role of anisotropy of membrane components in formation and stabilization of tubular structures in multicomponent membranes, PLOS ONE, 8 e73941, 2013.

#### Nanostructured diamond for Quantum applications

S. Mandal, E.L.H. Thomas, G. Klemencic, L. Gines, J. Werrell, S. Giblin, <u>O. A. Williams</u>\*

School of Physics and Astronomy, Cardiff University, Cardiff, UK \* <u>williamso@cardiff.ac.uk</u>

Diamond has a number of extreme properties such as the highest Youngs modulus, thermal conductivity, electrical resistivity of all materials etc, that make it very attractive for a plethora of applications ranging from cutting tools to single photon sources. Unfortunately, due to the phase diagram of carbon, diamond forms under pressures higher than 100 Kbar and temperatures greater 2000 K within the Earth. These conditions have been reproduced under laboratory conditions but are almost impossible to scale up to the large areas required for most applications. Diamond remains one of the hardest materials to grow synthetically.

Chemical Vapour Deposition of diamond was first accomplished around the same time as high pressure synthesis. This technique dissociates hydrogen and methane under high temperature plasmas to create atomic hydrogen and methyl radicals. The methyl radical acts as a building block for diamond growth, with non-diamond carbon being suppressed by the extremely aggressive atomic hydrogen background. This is a metastable process that is notoriously difficult to control.

However, thin diamond films can now be produced on substrates such as silicon with Young's modulus as high as 1100 GPa and high thermal conductivity. In this work the steps necessary to produce high quality diamond films for Micro-Electro-Mechanical Systems explained. Nucleation of diamond on foreign substrates, control over the CVD growth process, Chemical Mechanical Polishing and device fabrication will be demonstrated. Integration with materials such as AlN and GaN will be discussed. Superconducting and non-superconducting MEMS / SAW devices will be demonstrated with frequency-Q products as high as  $10^{14}$  Hz. The potential of diamond as material for Quantum metrology will be discussed.

# Chemical Vapour Deposition for the fabrication/modification of nanofiltration membranes

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There remains an interest in the use of membranes across the separations industry due to some favourable characteristics, namely, their simplicity in operation and control, avoidance of a phase change, and ease of scale up. Exploitation of the chemical properties of the membranes can enable more efficient separation processes compared to competitive techniques.

Polymeric membranes remain at the forefront of the industry due to their ease of fabrication and good scalability. Thin film composite membranes attract a large interest due to the ability to have greater control over the separation layer in comparison to asymmetric phase inverted membranes. Conventional membranes for liquid based separations in the nanofiltration range (<1000 g/mol) are formed via interfacial reactions. These give rise to hydrophilic membranes which are not well suited for certain solvents. Alternatively, polymeric coatings can lead to separating layers with greater hydrophobicity within the nanofiltration, but these can suffer from challenges of pore intrusion from the coating and involve reactions that lead to fairly undefined polymer networks. The use of catalysts can also be an unwanted trait when one is searching for a homogenous layer.

Chemical Vapour Deposition (CVD) and Plasma Enhanced Chemical Vapour Deposition (PECVD) are attractive alternatives for the fabrication of nanofiltration membranes. They enable a wide range of monomers to be utilised as the film forming species, whilst not bound to utilising specific reaction pathways when compared to films formed via interfacial polymerisation. "Cold plasma" PECVD is particularly useful when the substrates of interest are thermally sensitive. This is typically true for ultrafiltration membranes as they will suffer pore collapse upon heating.

Within this presentation, the fabrication of thin film composite membranes via CVD methods will be described. These membranes have been prepared for organic solvent nanofiltration, and comparisons are made to composite membranes prepared via more conventional thin film polymer membranes. The composite membranes have been characterised via their separation performance in organic solvents, SEM, contact angles, FTIR, and others.

### **Bioflexoelectricity and biohelielectricity**

#### Alexander G. Petrov

#### Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria agpetrov@issp.bas.bg

Four generalized degrees of freedom of a membrane: mechanical, electrical, optical and chemical, will be considered. The concept of a biomembrane that functions as a generalized electro-opto-chemi-mechanical mechanism, will be introduced. Direct and converse flexoelectric effects and photoflexoelectric effects of a biomembrane will be outlined in this respect.

Based on the bioflexoelectricity concept an attempt to create a membrane machine will be reported, as a model of a protocell. This model is based upon a photoactive giant vesicle membrane that contains curvature - or tension- gated ion channels. The functioning of this machine is quite similar to a classical steam engine, the steam pressure being replaced by pH gradient, the mechanical displacement by curvature (tension) variations and valves by curvature - or tension - gated ion channels.

The role of chirality of membrane - forming lipids is not well appreciated at present. Chirality of phospholipids makes fluid lipid bilayers helielectric, an effect we call biohelielectricity. Thus, chiral lipids would also play a central role in the functioning of cell membranes as active mechano-transducers. By periodically shearing and compressing nonaqueous lamellar phases of left (L-alpha-Phosphatidylcholine), right (D-alpha-Phosphatidylcholine) andracemic (DL-alpha-Phosphatidylcholine) lipids, we induced a tilt of the molecules with respect to the bilayer's normal and produced electric current perpendicular to the tilt plane and parallel to the membrane surface, but with the chiral lipids only. This coupling also allows for a wide variety of sensory possibilities of cell membranes such as mechano-reception, magneto-sensitivity, as well as in-plane proton membrane transport and related phenomena like ATP-synthesis, soft molecular machine performance, etc.

## Additive Manufacturing of metallic nanoparticles structures by 2-photons Direct Laser Writing

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Additive Manufacturing refers to a group of technologies that build physical objects directly from 3D Computer-Aided Design (CAD) data. In the field of nanotechnologies a the 2-photons Direct Laser Writing is the most advanced optical technique for creating arbitrarily complex 3D materials featuring details well below the diffraction limit, in organic resists.



The possibility to include metallic details or even to create metallic structures would pave the way for the realisation of metallic/polymeric nanocomposites for advanced optics.

Here we report about the study on the physical features of gold nano-particles created by 2-photons photo-reduction Direct Laser Writing in a polymeric or hydrogel matrix, doped with a suitable metallic precursor.

Our experiments are performed in a free surface drop cast or cell segregated thin film onto a glass substrate, in which we create 1D gratings made by stripes of GNPs with single or multiple laser sweep. We show that the stripe width increases with the laser power and the exposure time. We also analyse the influence of the exposure time over the created nano-particles size distribution and density and we show that by suitably adjusting the exposure time it is possible to maximize the frequency of a given diameter.

Finally, we report about preliminary experimental results aimed to elucidate the involved physical phenomena, beyond the optical absorption. In particular we point out the key-role of thermal and diffusive processes.

## Phospholipase A<sub>2</sub> induced remodeling processes on liquidordered/liquid-disordered bilayers mimicking cellular plasma membranes

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Vesicle cycling, which is an important biological event, involves the interplay between membrane lipids and proteins, among which the enzyme phospholipase  $A_2$  (PLA<sub>2</sub>) plays a critical role. The capacity of PLA<sub>2</sub> to trigger the budding and fission of liquid-ordered (L<sub>o</sub>) domains has been examined in palmitoyl-docosahexaenoylphosphatidylcholine (PDPC) and palmitoyl-oleoylphosphatidylcholine (POPC)/sphingomyelin/cholesterol membranes. They both exhibited a L<sub>o</sub>/liquid-disordered (L<sub>d</sub>) phase separation. We demonstrated that PLA<sub>2</sub> was able to trigger budding in PDPC-containing vesicles but not POPC ones. The enzymatic activity, line tension, and elasticity of the membrane surrounding the L<sub>o</sub> domains are critical for budding. The higher line tension of L<sub>o</sub> domains in PDPC mixtures was assigned to the greater difference in order parameters of the coexisting phases. The higher amount of lysophosphatidylcholine generated by PLA<sub>2</sub> in the PDPC-containing mixtures led to a less-rigid membrane, compared to POPC. The more elastic L<sub>d</sub> membranes in PDPC mixtures exert a lower counteracting force against the L<sub>o</sub> domain bending.

#### **Supercooled Soft Nanocomposites**

<u>S. Kralj</u><sup>1,\*</sup>, P. Kuryoz<sup>1</sup>, S. Rzoska<sup>2</sup>, Z. Kutnjak<sup>1</sup>

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Symmetry breaking is ubiquitous in nature and represents the key mechanism behind rich diversity of patterns exhibited by nature. In case of continuous symmetry breaking an order parameter consists of two qualitatively different components: an *amplitude* and *gauge field*. The latter component enables energy degeneracy and reveals how symmetry is broken. Inherent degeneracy could in general lead to nearby regions exhibiting significantly different gauge fields. Resulting frustrations can nucleate *topological defects* (TDs). These represent topologically stable localized nonlinear order parameter solutions.

Convenient systems to study patterns exhibiting TDs are various liquid crystalline (LC) phases. Due to their softness, fluidity and optical anisotropy&transparency TDs could be relatively easily experimentally generated and observed in them. Therefore, in LCs various theoretical predictions could be relatively easily tested. In this lecture we present our theory explaining supercooling driven glassy behaviour in systems exhibiting continuous symmetry breaking. Note that glass behaviour is still mysterious and several features remain unanswered despite intensive research in the respective field. In case of LCs we combine Kibble-Zurek (KZ) mechanism and Imry-Ma (IM) theorem to reproduce some characteristic features of general supercooling-driven glass behaviour. The KZ mechanism was originally introduced in cosmology to explain coarsening dynamics in the Higgs field in the early Universe. Furthermore, IM theorem was introduced in magnetism to explain impact of random field-type disorder on magnetic ordering. We show that combination of these well known mechanisms one could stabilise patterns of TDs, which macroscopically yield several glass-type characteristics.

# ORAL PRESENTATIONS

### Chromogenic smart nanocomposites as functional surfaces in energy efficient devices

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The presentation is related to chromogenic smart materials, based on transition metal oxide (TMO) nanocomposites, which due to their specific electronic structure are capable to express electrochromic (EC) effect. This effect was first observed in 1968, and was explained as a characteristic of a device varying the nano-composite optical properties when an external voltage triggers the EC material. The EC device modulates the optical transmittance in visible, and near infrared (NIR) when a low DC potential is applied. The device is considered as consisting of several layers deposited on conductive glass substrate.

The electroactive layers in an EC device switch between oxidized and reduced forms, leading to variations in optical transmittance. The EC functioning can be controlled by sunlight, temperature, or by thermal load. If a semitransparent photovoltaic (PV) cell is installed and provides the required activating electricity, then self powered windows can be developed. Electrohromic windows glazing is often replaced by other modern intelligent glazing options for energy savings purposes, like gazochromic windows, liquid crystal glazing [1].

The properties and fabrication of thermochromic (TC) VO<sub>2</sub> have been studied in the early 1970s. The most promising TC material for the windows is vanadium dioxide. It is known to exist in four polymorph forms: monoclinic VO<sub>2</sub> (M) and rutile VO<sub>2</sub> and two metastable forms by monoclinic to rutil transition temperature of  $68^{\circ}$ C [2].

The presentation reflects the results for smart chromogenic nanocomposites materials obtained by employing chemical vapor deposition processes, performed by the available in physical sciences institutes CVD equipments.

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#### Mechanism of lipidic pore formation by antimicrobial peptides

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Antimicrobial peptides are perspective agents for development of new generation of antibiotic drugs. They are known to recognize a bacterial cell membrane, bind to it and then form a through pore, thus resulting in cell death. Although all the stages are observed experimentally, the detailed mechanism of pore formation by the adsorbed peptides is still unknown. Antimicrobial peptides are presented by two major classes: i) amphipathic alpha-helical peptides; ii) peptides in beta-sheet conformation. In the present work we propose mechanism of pore formation by peptides of both classes.

Beta-sheet peptides electrostatically recruit charged lipids thus leading to formation of more ordered monolayer patch just beneath the adsorbed peptide. Alpha-helical amphipathic peptides are partially doused into the membrane monolayer. In both cases elastic deformations should appear in the membrane. To calculate the energy of deformations we utilized the theory of elasticity of liquid crystals adapted to lipid membranes. We accounted for deformations of splay, tilt, lateral compression/stretching under condition of local volumetric incompressibility of membrane monolayers. It was shown that at the initial membrane-bound stage it is energetically favorable for two peptides to adopt parallel orientation and stay at separations of about 6 nm. In this equilibrium configuration the membrane experiences the largest elastic stress right in the middle between the peptides. Assuming that the motion of the peptides is slow compared to rearrangement of lipid molecules we demonstrated that this position is optimal for formation of initial hydrophobic defect, which then develops to through lipidic pore. After formation of the pore the peptides occupy positions close to its equatorial plane leading to additional stabilization of the pore. The calculated energy barrier along the trajectory of pore formation is about 25 kBT, while the energy of the initial and the final states are close to each other. This means that the pore can be induced by just two molecules of antimicrobial peptides.

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## The regulation of membrane bending rigidity by components with high intrinsic curvature

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Cellular membranes contain lipids with different molecular geometry, which is characterized by the spontaneous curvature. It determines the preference of the lipid molecule to a particular geometry of the membrane surface. We showed here that the generation of bending deformations leads to a redistribution of lipids with high intrinsic curvature in accordance with their preferences. This redistribution results in decreasing of bending stress.

We have developed an approach that allows distinguish the instant elastic response of the membrane from the relaxation of the bending stress due to the redistribution of lipids with different geometry. The approach is based on an analysis of the process of rapid formation of membrane nanotubes (NTs) pulled from the bilayer lipid membrane. We apply this method to investigate the redistribution of curvature sensing protein, such as ENTH domain of protein epsin. We demonstrate that non-specific adsorption of ENTH on negatively charged BLM causes reduction of the radius of NT and bending rigidity of NT membrane due to redistribution of ENTH domain between NT and BLM surfaces. In addition, we measure the intrinsic curvature of lipid-protein complexes (their spontaneous curvature).

# Depot effect of bioactive components in experimental membrane filtrations

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A concomitant depot effects were found to be accompanying phenomena of experimental research nanofiltrations. Retardations of the researched type can hamper proper conclusions and deviate significantly the filtration results. Therefore we surveyed the effects of delayed membrane release of chlorogenic acid and caffeine, in a role of model compounds of interest for processed herbal products' recovery treatment. Fluxes and products' release were studied in course of 24 hours, both immediately after the initial filtration and after idle stay. Conclusions are drawn and recommendations advised for proper analytical membrane-related works.

## Investigation of photodynamic processes on the surface of bilayer lipid membrane by method of intramembrane field compensation (IFC)

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The method of photodynamic therapy is based on photosensitizers' (PS) ability to generate singlet oxygen, which oxidizes key molecules of cell membrane causing cell death. A prerequisite for the photodynamic effect is the PS adsorption on the cell membrane's surface. To test the photodynamic properties of PS the simplest model of lipid membrane, bilayer lipid membrane (BLM) with target-molecules of singlet oxygen di-4-ANEPPS, was used. Adsorption and destruction of the molecules have resulted in the boundary potential changes at the water/membrane interface which was detected by IFC method [1]. The rate of di-4-ANEPPS destruction is proportional to steady-state concentration of singlet oxygen in membrane upon illumination [2].

Sulphonated phthalocyanines (AlPcSn) and 4-sulphonatophenyl porphyrin (TPPS<sub>4</sub>) were studied. Potentials created by the PS adsorption were compared to zeta-potentials measured earlier [3]. The data of these two methods was similar for 3- or 4-sulfonated PS but disagreed for 1- or 2- ones. This disagreement was explained by existence of significant dipole moment in low sulphonated PS and by immersion of these molecules into the BLM which led to the membrane dipole potential appearance. The rate of the di-4-ANEPPS oxidation was proportional to the PS concentration at low concentrations, reaching the plateau at higher ones. This rate was higher for low sulfonated PS compared to high ones because of low ones' immersion into the region with higher concentration of oxygen. For TPPS<sub>4</sub> the adsorption potential and the ANEPPS destruction rate depended on pH with maximum at 5.5. The increase of potential up to pH 5.5 can be accredited to change of the membrane surface charge, consequent decrease - by an aggregation of TPPS<sub>4</sub> molecules.

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# Structural analysis of self-assembly of Influenza A virus protein scaffold

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Influenza A virus is an enveloped negative strand RNA virus from the Ortomixoviridae family. Its outer envelope is formed by bilayer lipid membrane, comprising incorporated glycoproteins haemogglutinin, HA, and neuraminidase, NA, along with proton channel M2. Inner shell of the virion is represented by membrane-associated scaffold of matrix proteins M1 contacting with viral ribonucleoprotein, RNP, lipid envelope and cytoplasmic tails of HA and NA. Influenza matrix protein M1 is known to possess multifunctionality. Apart from being a mechanical skeleton of a virion, it acts as a crucial factor for different processes, such as the release of viral RNA during infection and the budding of newly assembled virions. These processes take place at different pH conditions, so the function of M1 is also strongly dependent on pH. Therefore, it is of great interest to investigate the structural changes of M1 protein itself and viral protein scaffold under pH changing. For this reason we combined solution studies of full-length M1 protein using small angle X-ray scattering (SAXS) with atomic force microscopy (AFM) of protein layers on solid support to investigate processes of the protein selfassembly in the whole physiologically relevant range of pH, from 4 to 7. We revealed the tendency of M1 protein to form helical structures, even in acidic medium, and found that the threshold of transition from predominantly monomeric form of the protein to complete helical structures lies at pH around 6, while the structure of the individual protein molecule remains the same. We estimated the charge of M1 in the concerned range of pH and demonstrated that at pH of late endosome M1 significantly changes its charge meaning that electrostatics could be the main driving force in disassembly of Influenza A virus protein envelope. Modelling these processes using Derjagin-Landau-Verwey-Overbeek theory (DLVO) allows us to estimate the energy of M1-M1 interaction.

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## **Statistical Mechanics of Fluctuating Vesicle**

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The analysis of the thermally induced shape fluctuations of nearly spherical lipid vesicle is one of the most widely used methods for the determination of the bending elasticity modulus of the vesicle membrane. The theoretical basis of the method was developed by Milner and Safran [1].

The present work presents an investigation of the approximations, used by these authors in their theory. Estimation is done of the errors due to the mean-field approximation used in [1]. It is shown that contrary to the widely spread opinion, the theory of Milner and Safran describes best the membranes with very low stretching elasticity.

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## Structural Properties of Pre-formed DPPC and DSPC Lipid Vesicles: A Coarse Grain Molecular Dynamics

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The functionality of lipid vesicles is tightly related to their overall stability in biological environments. Here we address the thermodynamic behavior and the structural stability of pure lipid vesicles of either Dipalmitoylphosphatidylcholine (DPPC) or Distearoylphosphati-dylcholine (DSPC) in watery medium via molecular dynamics simulations. We have employed the GROMACS 4.x package in conjunction with the MARTINI coarse grain force-field to perform our computations. To achieve construct pre-formed vesicles we designed a script to construct in advance general initial configurations with different shapes. We have shown that the pre-formed DPPC and DSPC vesicles remain thermodynamically stable throughout the simulation time, although the time step needed to solve the equation of motion for DSPC vesicles is several orders of magnitude smaller than that for DPPC. The success of the proposed approach enables us to "build" an initial simulation set of vesicles and to shorten the the simulation time significantly.

For more details see reference [1].



Initial configuration containing 2704 DSPC molecules constructed via our MATLAB code.

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#### Boundary potential of lipid bilayers: methods and interpretations

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Electric field at the boundaries of cell membranes consists of two components - the diffuse part of the electrical double layer and the potential drop over polar area inside the membrane itself. The latter potential is generally attributed to dipole effects and depends on the lipid hydration and phase state. The change of dipole potential reports any alterations in these conditions which are important for membrane elasticity and have effect on conformation mobility of membrane proteins. This report expands the previous one presented in the Conference. It focused mostly on the experimental approaches developed to detect the relation of dipole effects with the bilayer structure and to study their molecular nature. Total boundary potential (BP) of planar bilayer lipid membranes (BLM) can be controlled by Intramembraneous Field Compensation (IFC) method developed in our laboratory [1]. This method combined with traditional electrokinetic measurements in liposome suspension allows us to detect significant changes of dipole potential induced by adsorbed multivalent cations ( $Be^{2+}$ ,  $Gd^{3+}$ ), synthetic polycations and polypeptides [2]. The alternative method is applied to Langmuir lipid monolayers. It was found that Volta potential registered at lipid monolayers and their elasticity are directly correlated [3]. Multivalent inorganic cations increase the dipole potential by 100-150 mV and make the membrane rigid [4]. Most of these observations were simulated by methods of Molecular Dynamics. To compare MD systems with the real ones the "electric interface" of bilayer was associated with the maximum in distribution of low-affinity counterions at the membrane-water interface. Then the dipole potential was deduced from BP and different structural factors (lipid structure, water orientation, ion adsorption etc.) responsible for this component were analyzed in many details [5]. Two principal factors contribute to BP - water and lipid molecules - and two opposite effects in BP dipole component visualized by MD simulation: the positive effect due to an inorganic cation penetration into the polar area of BLM and the negative one in the presence of lysine attributed to changes in the number of H-bonded water molecules with the lipid phosphate group [2]. In addition, the multivalent cation clearly coordinates 2-3 adjacent lipid molecules and, thus, initiates lateral condensation of lipids. This phenomenon was assumed to be the key reason of the blocking effect of  $Gd^{3+}$  on *E.coli* mechanosensitive channels incorporated to BLM composed of PS molecules [4].

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## Novel Hydrazones – Antioxidant Potential and Stabilization via Polysaccharide Particle

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Hydrazones are widely studied biologically important compounds associated with broad spectrum of biological activities. i.e. antibactial, anticancer, anti-inflammatory, antioxidant etc. The preservation of the established activities is important in view of their future use.

In this study, we aimed to: i) determine the impact of three new hydrazone derivatives in *in vitro* systems used to investigate free radical processes - radical scavenging approach (ABTS and DPPH) and iron induced peroxidation in lipid containing model systems and ii) evaluate the potential of polysaccharide-based particles to act as protective carriers preserving the antioxidant activity (AOA) of the tested compounds.

To achieve these aims a series of isonicotinoyl hydrazones – salicylaldehyde benzoylhydrazone (SBH) derivatives were used (5-bromosalicylaldehyde isonicotinoylhydrazone (5BrSIH), 3-methoxysalicylaldehyde isonicotinoylhydrazone (3mSIH) and 4-methoxysalicylaldehyde isonicotinoylhydrazone (4mSIH)). The tested compounds were encapsulated in chitosan-alginate particles by inotropic gelation method and a comparative evaluation of the antioxidant properties of the encapsulated and non encapsulated hydrazones during 30 days was performed.

The tested compounds revealed excellent antioxidant effectiveness in the ABTS system. In the DPPH radical scavenging assay the compounds exhibited very weak (3mSIH and 4mSIH) or absence (5BrSIH) of AOA. The data from the iron induced peroxidation methods disclosed better antioxidant properties of the derivatives in the system containing egg yolk lipoproteins which is more plausible compared to the lecithin containing one.

The incorporation of bromine atom on  $5^{\text{th}}$  position in salicylaldehyde moiety is associated with diminishment of the radical scavenging activity in the systems containing stable free radicals but its AOA reduction after encapsulation during the storage was only 9.17%. The obtained data indicate that compounds have proven themselves as promising candidates for further evaluation as antioxidant agents. Their encapsulation in chitosan-alginate particles could be a useful approach for improving the stability of their antioxidant properties.

# POSTERS

## Synergetic effect of TiO<sub>2</sub> nanofillers and NaIO<sub>4</sub> additives on conductivity and dielectric properties of PEO/PVP nanocomposite electrolytes for electrochemical cell applications

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Solid-state nanocomposite polymer electrolytes have attracted great attention by the researchers in the field of rechargeable metal-ion battery applications to overcome a great deal of drawbacks of conventional liquid electrolytes especially related to safety issues originating from their high volatility and flammability. Substantial research, development, and demonstration efforts are currently in progress to develop sodium ion conducting electrolytes and compatible electrode materials for practically viable SIBs [1]. Investigations on sodium-ion conducting polymer blend electrolyte systems based on PEO/ PVP complexed with NaIO<sub>4</sub> salt and TiO<sub>2</sub> nanofillers were presented in this report. The complexed polymer blend electrolytes were prepared in the form of dimensionally stable and free-standing films by solution cast technique. FTIR and XRD studies confirmed the miscibility between PEO and PVP and the complexation of the salt with PEO/PVP polymer host. SEM and TEM measurements were carried out to study surface morphological features and to evaluate size & distribution of the dispersed TiO<sub>2</sub> nanofillers. Complex impedance spectroscopy in the frequency 1 Hz - 1 MHz within the temperature range 303 K - 343 K. Ionic conductivity increased with the increase of salt concentration as well as temperature. Upon addition of TiO<sub>2</sub> nanofillers to electrolyte system, it was found to result in the enhancement of ionic conductivity. Dielectric and electric modulus of the blend PEO/ PVP/Na+ electrolytes were analyzed in order to understand the influence of TiO<sub>2</sub> nanofillers on long range and short range dynamics of ions.

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#### Electro-optical and dielectric characterization of nano-PDLC films

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This report concerns thin films (25  $\mu$ m thickness) of polymer-dispersed liquid crystal (PDLC) composites having submicrometer-sized nematic droplets. The nano-PDLC films were prepared by performing photo-induced phase separation of mixed soft material composed from the room-temperature nematic liquid crystal 4-*n*-heptyl cyanobiphenyl (7CB) and photo-curable polymer NOA-65. Being of interest for various photonics and electro-optical (EO) applications driven by alternating-current electric field (e.g., efficient shutters, amplitude-frequency and spatial modulators and filters), the produced nanocomposites were studied by EO measurements and complex impedance spectroscopy. By means of the latter, the dielectric characteristics of the examined 7CB/NOA-65 nano-PDLC were obtained within the frequency range from 1 mHz to 100 kHz of the driving electric field. The experimental data were analyzed by applying the Havriliak-Negami model [1,2] to get information about the molecular dynamics of this nano-confined nematic, useful for optimizing its EO performance.



**Figure 1.** Frequency-dependent real (a) and imaginary (b) parts of the complex dielectric permittivity measured for the 7CB/NOA-65 nano-PDLC studied here.

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### Advanced atmospheric investigations at basic environmental observatory "Moussala"

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Global climate changes, cosmic rays, trans boundary and local pollution are the main areas of research performed in regional Global Atmospheric Watch (GAW) station BEO Moussala (2925 m a.s.l., 42°10'45" N, 23°35'07" E). Real time measurements and observations are performed in the field of atmospheric chemistry and physics. Complex information about aerosols is obtained by using three-wavelength integrating Nephelometer for measuring the scattering and backscattering coefficients, continuous light absorption photometer and by the scanning mobile particle sizer. Cloud condensation nuclei counter measures aerosol particles that can form into cloud droplets. The system for radioactivity and heavy metals in aerosols measurement gives the opportunity to monitor a large scale radioactive aerosol transport.

Gamma background measurements and the spectrum of gamma-rays in the air near Moussala peak are carried out in real time. HYSPLIT back trajectory model is used to determine the origin of registered by apparatus data. Forecast for air mass trajectory calculated by the DREAM code is used also. The obtained information combined with a full set of corresponding meteorological parameters is transmitted via a high frequency radio telecommunication system to the Internet.

## Photoresponsive azo-doped Aerosil/7CB nematic liquid-crystalline nanocomposite films: the role of polyimide alignment layers of the films

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We studied thin films (25  $\mu$ m-thick) of nanomaterials composed from 3 wt% Aerosil nanospheres and the room-temperature nematic liquid crystal 4-*n*-heptyl cyanobiphenyl. The inclusion of 3 wt% of the photoactive liquid crystal 4-(4'-ethoxyphenylazo)-phenyl hexanoate in these nanostructured nematics make them photoresponsive [1]. The films had alignment layers from polyimide (PI). Our study is concentrated on the PI-role for the photo-stimulated electro-optical properties of the examined nanocomposite films.

For azo-doped Aerosil/7CB nanocomposite films studied here, the presence of unidirectional rubbed PI alignment layers is of paramount importance for the effect of UV photo-driven stimulation of their electro-optics. The UV light-induced change in the transparency of the films is closely related to the alignment in the bulk, owing to the PI layers. An UV light-induced change of anchoring conditions due to space charge generation by the PI layers (close to the PI surfaces) is also possible to contribute to the UV-light-modified electro-optics of such photoresponsive nematic systems, but the role of this mechanism is much less.

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#### Double helices in chiral smectics under electric field

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Behavior of double helices (DH\*) formed in the temperature interval N\*-SmA\* in compounds of non-chiral liquid crystal doped with chiral molecules is investigated. Two different systems presenting left-handed or right-handed chirality are studied. A statistics of the DH\* handedness reveals the same sign as that of the macroscopic chirality of the enantiomers' SmA\*, as predicted theoretically in [1]. Application of a successively increased AC electric field at fixed temperature decreases the pitch of the DH\*s, due to the shrinking of the diameter of the cylinder containing them, thus satisfying the Darboux law. This effect was similar to that produced by the decrease of the temperature in absence of the field. The evolution of the pitch of a DH\* as a function of the intensity of the electric field and as a function of the time duration of the field with a constant amplitude is studied by optical microscopy observations.



Illustration of DH\* behavior in electric field

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#### **Electrochemical impedance spectroscopy of YBCO ceramics**

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In recent years intensive studies on YBCO system ceramics with varying compsition such as Y-156, Y-13-20-33, etc. have been conducted [1,2]. With the aim of a practical application electrochemical impedance measurements were done on two cuprate ceramic tablet samples with nominal composition YBa<sub>5</sub>Cu<sub>6</sub>O<sub>x</sub> and Y<sub>13</sub>Ba<sub>20</sub>Cu<sub>33</sub>O<sub>x</sub> obtained through solid state reaction, in a 7M KOH solution. Using the electrochemical system SP-200 potentiostat/galvanostat the frequency scan range was set from 2 MHz to 10 mHz. Tests were conducted at different applied sinusoidal voltages (5, 10, 20, 50, 100, 200, 300, 500 mV vs SCE). The working electrode is the sample, glued to a steel plate with conductive silver paste. The steel plate is insulated from the electrolyte with paraffin wax so that only one face of the tablet is in contact with the solution. The counter electrode is a polished platinum plate. Potential is measured relative to a saturated calomel electrode (SCE). Obtained results show that in the frequency range from 20 kHz до 2 MHz the absolute value of the impedance exhibits linear behavior. For the Y-156 sampleit decreases fom 150 to100 ohms. Y-13-20-33 displays much lower impedance (2-40hms) in that frequency range.Current studies suggested the practical potential of YBCO systems for energy storage nanotechnology such as long-life electrode material for rechargeable batteries.

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#### Dielectric study of azo-doped aerosil/7CB filled nematic upon UV light

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We studied nanocomposite produced from nano-filled nematic by doping with 3 wt.% photoactive azobenzene liquid crystal 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH). The photo-insensitive host nanocomposite material (the filled nematic) was a gel formed from the nematic 4-n-heptyl cyanobiphenyl (7CB) and 3 wt.% of silica nanospheres (Aerosil 300) of size ca. 7 nm. It is of research interest to be analyzed the dielectric behavior of this photo-responsive nanostructured nematic system as exposed to UV light at the wavelength of 375 nm. The latter falls in the  $\pi - \pi^*$  absorption band of *trans* conformers of EPH azo-bonded molecules that decorate the network formed within the aerosil/7CB. If the UV light intensity is high enough, the dipole moment of the azobenzene group can be reversibly switched between approximately from 0 (for *trans*) to 3 D (for *cis* conformers). We applied the electrochemical impedance spectroscopy (Figure 1) to determine the UV-light-produced effect upon continuous *trans*-to-*cis* photoisomerization of EPH molecules by varying the UV light intensity.



**Figure 1**: Rough data obtained by impedance spectroscopy: (a) real and (b) imaginary parts of complex impedance measured for the studied azo-doped nano-filled nematic.

#### Acknowledgements

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#### **Rheological properties of erythrocyte suspensions**

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Red blood cells (RBC, or erythrocytes) constitute the main cellular component of normal blood. Their deformability and rheological properties are of particular importance for blood circulation and physiology [1, 2]. In human body the average value of hematocrit (the volume of packed RBCs relative to the blood volume) is around 45%. Rheological studies on concentrated (with cell volume fraction higher than 10%) RBC suspensions are informative and useful for various biomedical applications. Measurements accounting for the individual dynamics of cells are also indicative of cytoskeleton-related phenomena and alterations of the cellular elasticity [1].

In concentrated red blood cell suspensions the individual cell dynamics in flow is altered by the hydrodynamic interactions between cells. The effective viscosity of erythrocyte suspensions is obtained to capture cell dynamics similarly to the dilute limit. A hysteresis effect is found for the effective viscosity as a function of the shear rate under moderate shear stresses, at which swinging of RBC is expected [3, 4]. The higher the volume fraction of erythrocytes is, the stronger this dependence is reported.

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## Sugar effect on lipid membranes measured by flicker spectroscopy, electrodeformation and electroporation of lipid vesicles

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Bending elasticity, edge tension and electrical capacitance of lipid bilayers [1] were measured in aqueous environments containing sugars. Flicker spectroscopy [2] of nearly spherical giant unilamellar vesicles (GUVs) showed softening of palmitoyl-oleoyl phosphatidylcholine (POPC) membranes in the presence of sucrose. Membrane electroporation was used to quantify the edge tension of POPC bilayers. Strong electrical pulses (60-80 V/mm) with short duration (5 ms) were applied to induce pores in GUVs [3]. Pore resealing was studied for vesicles in aqueous solutions containing from 0 to 400 mM of sucrose or glucose. The edge tension of lipid bilayers was found to decrease with increasing the sugar content in the aqueous environment. Membrane capacitance was measured by electrode formation of GUVs [4] under AC fields (0.5-10 kHz) in aqueous solutions with up to 200 mM of sucrose. The conductivity of the solutions inside and outside the vesicles was adjusted by addition of sodium chloride. A possible alteration of the electrical properties of lipid membranes is suggested to explain the dependence measured for the membrane capacitance with the sucrose concentration in the water.

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## Surface plasmon for exploration the temperature dependence of hybrid cholesteric liquid crystal's pitch

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Knowledge of the molecular director profile near to the boundaries of a liquid crystal (LC) cell and its dynamic behaviour under external influence is very useful for device design. For getting the need information the surface plasmon resonance (SPR) is used [1-3]. In this study we experimentally track the temperature dependence of the pitch of hybrid cholesterc LC by the SPR spectral shift. The excitation of SPR is usually based on a prism coupling configuration. Metal gratings are also used for supporting surface plasmons and provide an alternative design of SPR excitation. For many applications gratings are more feasible. In our previous study [4] we optimized some parameters related to SPR excitation on grating for developing the structure for application.

Based on this experience, in present work we use a gold grating as bottom wall of liquid crystal (LC) cell. The top wall is a BK7 glass plate. The LC is induced hybrid cholesteric. The nematic matrix is commercially available E7, while the chiral supplement is S811. A prior work was done for finding an optimal concentration of S811, the corresponding pitch and its temperature dependence.

Two strips with thickness about 12  $\mu$ m are used as the cell gap spacers and the cell is capillary filled with induced hybrid cholesteric at optimal ratio nematic/cholesteric. Experimentally are provided indispensable condition for homogeneous alignment of LC's molecules. The temperature of LC cell is controlled in 30 – 60 °C. The observation of SPR is provided by spectral read-off. The spectral shift versus temperature is studied. The results are compared with the LC cell measurements provided by a polarization microscope. The conclusions about the director orientation and pitch are formulated. The possibility about the application of studied structure for a temperature sensor is discussed.

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## Cytotoxic effects of Co<sub>1-x</sub>Mn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> ferrite nanoparticles synthesized under non-hydrolytic conditions (Bradley's reaction) - *in vitro*

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Ferrite spinel nanoparticles (Co<sub>1-x</sub>Mn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub>) characterized by the mean crystallite size of 10 nm were prepared using a microwave stimulated Bradley's technique under nonhydrolytic conditions. Magnetic properties of this material have been studied using magnetization measurements in a temperature range from 5 to 350 K and in fields up to 90 kOe. For samples investigated (x = 0.2, 0.5, 0.8) two characteristic features have been observed: systematic decrease of the saturation magnetization with increasing temperature, which is typical for bulk ferrites, and almost completely reversible M(H)loop at T = 320 K. The saturation magnetization has decreased also with decreasing amount of Co, but at the same time the coercive force has changed non-monotonically. This observation seems to be a characteristic property of the nanoparticle form of the material we have studied. Our results show that increasing the amount of Mn in a nanocrystalline compound Co<sub>1-x</sub>Mn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> changes its magnetic properties from the magnetically hard to magnetically soft, as for bulk materials. Structural, chemical and morphological characterizations were performed using XRD, SEM-EDS and TEM techniques. Stability of the nanoparticles and their tendency to form agglomerates were tested using DLS technique exploiting the effect of different biological environments and protein stabilization. It was shown that the BSA adsorption depended on the concentration and nanoparticle chemical composition showing higher affinities to the higher cobalt/manganese ratio. Cytotoxicity assessment of non-surface blocked Co<sub>1</sub>.  $_{\rm x}$ Mn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles was done for the phagocytic murine macrophage (J774.E), cancer fibroblast human osteosarcoma (HTB) as well as mesenchymal stem cells derived from human adipose tissue (ASCs). The results indicate that the cytotoxic response strongly depends on particle concentration as well as type of the cell lines.

#### Acknowledgements

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## Surface characterization and orientation interaction between diamond-like carbon layer structure and dimeric liquid crystals

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Diamond-like carbon (DLC) and amorphous carbon films are very promising type of semiconductor materials. Depending on the  $sp^2/sp^3$  ratio, the material band gap varies between 0.8 and 3 eV. Moreover carbon films possess different interesting for practice properties: comparable to the Silicon, Diamond like structure has 22-time better thermal conductivity etc. Here we will present one type of implementation of such type nanostructure.

One attempt for orientation of dimeric LC by using of predeposited DLC layer with different ratio of sp<sup>2</sup>/sp<sup>3</sup> hybridized carbon content. It could be expected a pronounced  $\pi 1-\pi 2$  interaction between SP levels on the surface and dimeric ring of LC.

We will do comparison of surface anchoring strength of both orientation surfaces: with predeposited DLC and SWCNT layers. It will be shown the mechanisms of interaction of dimeric LC and activated surfaces with DLC and SWCNT. In both cases we have  $\pi$ - $\pi$  interaction, which is in addition to the Hydrogen bonding.

The Hydrogen bonding is with medium strength, comparable to the Covalent and Wan der Vaals type of molecular connections. It was observed a good alignment of dimeric LC by using of predeposited SWCNTs.

Raman spectroscopy data evidenced the presence of charge transfer between contacting hexagonal rings of CNTs and the C = O groups of the LC molecules. The effect of alignment was explained by the  $\pi$ - $\pi$  stacking and charge transfer.

## Investigation of the structure and thermal behaviour of polymer liquid crystal/single wall carbon nanotubes nanocomposites

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In the present work nanocomposites of polymer liquid crystal poly(heptane-1,7-dyil biphenyl-4,4'-dicarboxilate), P7MB, and single-wall carbon nanotubes (Meijo company), SWCNT, were prepared by solution mixing. First, the P7MB was dissolved into chloroform at room temperature by bath sonication. Separately, SWCNT suspension was prepared by mixing the nanotubes with chloroform. The suspension was tip-sonicated for 30 minutes and then bath-sonicated for 4 hours. The P7MB solution and SWCNT suspension were then mixed and again bath sonicated for 4 hours. From the final suspension films were casted, where the solvent was left to evaporate overnight in a vacuum oven at room temperature. The films were then thermally treated (quenched, annealed, or cooled and heated with a constant rate). The structure and thermal behavior of the nanocomposites were investigated by means of real-time X-ray scattering and differential scanning calorimetry, DSC.

The results from DSC show two phase transitions on cooling and single one on heating. Hence, the smectic order of P7MB is preserved in the nanocomposites as well as its monotropic behaviour. The transition temperatures of smectic phase formation are several degrees higher than those of the neat polymer. They range from 149.22 (at a rate 2 °C/min) to 141.7 (10 °C/min). The smectic phase seems to crystallize on further cooling at temperatures about 111.07  $\div$  86.26 °C in a two-step-process. The melting endotherm appears as a two-step-process also, at temperatures in the range from 157.34 to 166.65 °C (at heating rate 10 °C/min). The shift in the melting temperature is higher at lower cooling rates. By means of real-time x-ray scattering the smectic layer spacing is estimated to be about 1.73 nm and it shifts to higher values at cooling and depending on temperature treatment. The temperature, at which the smectic peak appears on cooling agrees well with that obtained from DSC.

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# The unique physical properties of the hydrogen bonded in dimers liquid crystals

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The dimerization of aromatic carboxylic acids, is the base of the structure formation of hydrogen bonded in dimers liquid crystals (HBDLCs) that exhibit non-conventional mesomophism. The structural units of these LCs are amphiphilic-type molecules, which after suitable functionalization, induce supramolecular complexes, nanocomposites based on HBDLCs. The liquid crystalline character of the nanocomposites strongly dependent on intermolecular hydrogen bonds between symmetric, where the H-donors and H acceptors are contained in similar and non-symmetric HBDLCs, where the Hdonors and H acceptors are contained in unlike molecules. The self-assembly of carboxylic acid components of HBDLCs and mesogenic and non-mesogenic nanoparticles, that function as H-bond donors and acceptors, respectively, results in the formation of a wide variety of liquid-crystalline low molecular weight mesogenic complex structures. The strength and non-covalent character of the hydrogen bonds provides both sufficient HBDLCs complex stability and bonding flexibility with a possibility to design and drive the supramolecular geometry. By adopting such nonlinear geometries, low molar mass HBDLCs and in particular polymeric suprastructures, due to its high specificity and directionality, exhibit new strong photoresponsible ferroelectric phases with a large significance for application as tunable electro-optical components in the photonic devices. We investigated a series of nanocomposites produced by mixture of HBDLC, (4, alkyloxybenzoic acid-with homologue number n=7, 70BA) serving as matrices, with non-mesogenic (functionalized single walled carbon nano-tubes-f,SWCNTs, hydroxypiridine-HOPY, perfluorooctanoic acid-PFOA) and mesogenic (cholesteric benzoate-ChB) nano-particles in various shapes and sizes.

Using micro-textural polarization, DSC thermal and X-ray analyses, a set of new chiral ferroelectric phases were found in the nanocomposites, otherwise do not appearing in the pristine achiral HBDLCs materials. The conformability, the intra and intermolecular interactions, of the HBDLCs matrix and doped nano-particles were indicated and analyzed by both polarization FT far infrared (FTfIR) and micro-Raman spectroscopies. A molecular model of an unique low-temperature ferroelectric smectic phase ( $S_G$ ) based on the molecular dimer ring symmetry reduction (bent dimer formation) towards to the lowest triclinic one is presented.

## Transition metal oxides core-shell nanocomposites prepared by combination of various techniques with atomic layer deposition for photocatalytic, electrochromic and gas sensing applications

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Transition metal oxides are widely applied for photocatalytic, electrochromic and gas sensing applications. Their properties might be improved by making composites of them with other semiconductor oxides. In the present research, two approaches to prepare core-shell nanocomposites of several transition metal oxides were used. By combining controlled annealing and atomic layer deposition (ALD), pure WO<sub>3</sub> and core/shell WO<sub>3</sub>/TiO<sub>2</sub> nanoparticles were prepared and tested as photocatalysts and electrochromic materials. Bare ZnO and TiO<sub>2</sub>, as well as core/shell ZnO/TiO<sub>2</sub> and TiO<sub>2</sub>/ZnO nanofibers were prepared by electrospinning, annealing and ALD, and their photocatalytic and gas sensing properties were tested. The morphology, composition and structure of the pure and composite nanoparticles and nanofibers were also characterized by SEM-EDX, TEM, XRD, UV-Vis, FTIR and Raman. It was investigated how these semiconductor oxides interacted with each other when a pure oxide particle or fiber was covered with an ultra-thin film of other oxide and how combining thece core and shell materials influenced their properties in photocatalysis, electrochromism and gas sensing.



TEM image of core/shell WO<sub>3</sub>/TiO<sub>2</sub> nanocomposite.

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