

The 3rd Polish-Slovenian International Seminar on Soft Matter
26th-28th September 2024

SCIENTIFIC SESSIONS



The 3rd Polish-Slovenian International Seminar on
26th - 28th September 2024



The 3rd Polish-Slovenian International Seminar on Soft Matter:

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OPENING LECTURE

Analogue of “virtual particles”

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Abstract: There is strong evidence that many natural phenomena could be described using geometrical approaches. Furthermore, the discovery of the Higgs boson confirmed that the entire Universe is pervaded by the Higgs field, suggesting that physical fields represent the fundamental natural entities. Consequently, it is of interest to identify experimentally accessible systems in which the universality of geometry-based approaches could be tested or/and investigated in detail. Testbed laboratory systems could serve as gateways to a deeper understanding of phenomena in other, hardly or even experimentally accessible systems that are mathematically related to such analogs.

Diverse liquid crystalline (LC) phases and configurations are ideal candidates for such purposes. These optically anisotropic soft matter representatives combine properties of ordered crystals and liquids, and exhibit the rich diversity of different symmetries. Their states could be well described by mesoscopic molecular fields that are easily manipulated by diverse external stimuli, and the resulting field configurations could be probed using relatively inexpensive and straightforward optical methods (e.g. optical polarizing microscopy).

In this presentation, I intend to illustrate how phenomena studied in LCs could be exploited to get insight into open problems of particle physics and cosmology. I address the stabilization and manipulation of skyrmion-family structures (these quasiparticle configurations were originally proposed to describe hadrons and mesons), the stabilization and manipulation of fermionic Weyl-type excitations, and illustrate analogs of “virtual particles”.

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Honorary Lectures

- ♠ Prof. Ivan I. Smalyukh — USA
- ♠ Mitja Slaviniec — Slovenia
- ♠ Prof. Alexander Umantsev — USA
- ♠ Prof. Atsushi Yoshizawa — Japan
- ♠ Prof. Kinga Pielichowska — Poland
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Sustainability with Knotted Chiral Meta Matter

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Abstract: Well before topology existed as a formal branch of mathematics and long before the very existence of atoms was widely accepted, Lord Kelvin hypothesized that chemical elements in the Periodic Table were different vortex knots tied within the so-called “aether”. These ideas gave origins to an entirely new branch of mathematics, and the very need of distinguishing different chiral knots led to the celebrated Kelvin's definition of chirality. Kelvin's vortex-atom theory turned out not to describe the real-world atoms, and the “aether” was found not to exist, but the idea of knots in physical fields behaving like particles became pervasive in many branches of physics, including in various models of subatomic particles.

This lecture will describe how we experimentally and theoretically realize microscopic analogs of Kelvin's vortex atoms in chiral ordered media, like liquid crystals, colloids, and magnets. Endowed with topological protection, our vortex knot quasi-atoms undergo fusion and fission, similar to the counterparts of these processes exhibited by atomic nuclei, as well as self-assemble into a plethora of different crystals that then exhibit unexpected properties like giant electrostriction. While vortex knots were previously generated in nonchiral media like conventional fluids, they were found to undergo a series of reconnections in the vortex lines that eventually made the entire knots disappear. Our vortex knots in the chiral ordered host medium are stabilized by the combination of medium's chirality and topological protection of the particle-like objects they correspond to. The chiral condensed matter host media serve a role analogous to that of the fictional “perfect fluid”, the other that was never found to exist. We demonstrate and envisage many types of similar topology-protected atom-like quasi-particles as building blocks of pre-designed forms of an artificial matter, the knotted chiral meta matter capable of overcoming limitations of the natural world around us. Technological uses may range from spintronics and data storage to new breeds of electro-optic devices and displays, and even to storing energy in laser beams of light tied into knots by knotted vortices. A new international institute, the WPI-SKCM², is now on a mission to use chirality at all scales of the natural hierarchy in order to make new forms of meta matter, knot by knot.

Keywords: Kelvin's vortex-atom theory, chiral condensed matter

References

- [1] Zhao, H., Boris A. Malomed, B. A., Smalyukh I. I. Topological solitonic macromolecules, *Nature Communications*. 2023, 14, 4581, 1-12. <https://doi.org/10.1038/s41467-023-40335-5>
- [2] Tai, J-S. B., Smalyukh, I. I. Three-dimensional crystals of adaptive knots. *Science*. 2019, 365(6460), 1449-1453. doi: 10.1126/science.aay1638
- [3] Ackerman P. J., Smalyukh I. I. Static three-dimensional topological solitons in fluid chiral ferromagnets and colloids, *Nat. Mater.*. 2017, 16(4), 426-432. doi: 10.1038/nmat4826
- [4] Tai, J-S B., Hess, A. J., Wu, J-S, Smalyukh, I. I. Field-controlled dynamics of skyrmions and monopoles. *Science Advances*. 2024, 10(4). doi: 10.1126/sciadv.adj93

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Domain-like structures in physical fields

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Abstract: We consider history-dependent behavior in domain-type configurations in physical fields exhibiting orientational order that are formed in configurations reached via continuous symmetry-breaking phase transitions. In equilibrium, these systems exhibit in the absence of impurities a spatially homogeneous order. We focus on cases where domains are formed via (i) Kibble-Zurek mechanism in fast enough quenches or by (ii) Kibble mechanism in strongly supercooled phases. These mechanism were originally introduced to model coarsening dynamics of the Higgs field in the early universe. In both cases, domains could be arrested due to pinned topological defects (TDs) that are formed at domain walls. TDs refer to localized field distortions that are topologically protected. Note, that TDs in a relevant physical field might correspond to “fundamental particles” if fields represent fundamental natural entities. In systems exhibiting polar or quadrupolar order point and line defects (disclinations) dominate, respectively. In particular, the disclinations could form complex entangled structures and are more efficient in stabilizing domains. Domain patterns formed by fast quenches could be arrested by impurities imposing a strong enough random-field type disorder, as suggested by the universal Imry-Ma theorem. On the other hand, domains formed in supercooled systems could also be formed if large enough energy barriers arresting domains are established due to the large enough systems’ stiffness. The resulting effective interactions in established domain-type patterns could be described by random matrices. The resulting eigenvectors reveal expected structural excitations formed in such structures. The most important role is commonly played by the random matrix largest eigenvector. Qualitatively different behavior is expected if this eigenvector exhibits a localized or extended character. In the former case, one expects a gradual, non-critical-type transition into a glass-type structure. However, in the latter case, a critical-like phase behavior could be observed.

Keywords: topological defects, phase transition, Kibble-Zurek mechanism

References

- [1] Zurek, W. H., Cosmological experiments in superfluid helium? *Nature* .1985, 317, 505-508. doi: 10.1038/317505a0
- [2] Kibble, T. W. B., Topology of cosmic domains and strings, *J. Phys. A: Math. Gen.* 1976, 9, 1387-1389. doi: 10.1088/0305-4470/9/8/029
- [3] Imry, Y., Ma, S. Random-field instability of the ordered state of continuous symmetry, *Phys. Rev. Lett.* 1975, 35, 1399-1401. doi: <https://doi.org/10.1103/PhysRevLett.35.1399>

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Two-step mechanism of macromolecular nucleation and crystallization: field theory and simulations

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Abstract: Many biological substances do not follow the traditional Gibbsian mechanism of nucleation, in which a critical nucleus of a particular size and crystalline structure appears in the melt or a solution, followed by subsequent crystal growth. Instead, they follow the two-step mechanism of nucleation and growth of crystals, which consists of the formation of a dense precursor in the liquid phase (step 1) and the subsequent formation of a crystalline phase inside the precursor (step 2). The two-step mechanism can be found in the cases of crystallization of colloidal particles, proteins, calcium carbonate biomineral, conjugated polymers, and other macromolecules.

In this presentation, I will discuss the phase-field method of simulations of crystallization of macromolecules from solutions¹, which provides a good combination of efficiency, thermodynamic consistency, and predictive capability. The method allowed us to address some of the open questions of protein crystallization. The phase diagram of the solution contains low-density and high-density liquid and solid phases, with the low-density liquid being the initial solution and the high-density solid - the final crystal. We observed three steps of the transformation process (see Figure), where the first step was homogeneous nucleation of the intermediate high-density liquid droplets, the second step was heterogeneous nucleation of the crystals on the droplet's surface, and the third step was dissolution of some of the crystallites and dense liquid droplets back into the liquid state of low density. We found the thermodynamic criterion for two-step nucleation, which states that there is a gap in the overall initial solution concentrations below the liquidus, where the one-step process is thermodynamically impossible. Beyond the gap, we observed a one-step transformation, which ended up with the formation of a phase morphologically similar to a gel. At large values of the liquid interaction coefficient and moderate values of the overall concentration, we observed the transformation scenario, which was reminiscent of the amorphous phase formation. The simulation results allowed us to suggest a resolution of the George-Wilson problem as the lack of dense liquid droplets for weak macromolecular attraction and ease of amorphous phase formation for the strong attraction.

Keywords: simulation, amorphous phase, two-step mechanism

References

[1] L'vov P. E., Umantsev A. R. *Cryst. Growth Des.* 2021, 21, 366–382. <https://doi.org/10.1021/acs.cgd.0c01224>

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Liquid-crystalline supermolecules inducing layer fluctuations: from hierarchical to dissipative structures

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Abstract: Liquid crystal materials, which have both liquid and solid properties, inevitably exhibit fluctuations. Therefore, fluctuations are characteristic phenomena of liquid crystals and their phase transitions, so the understanding of fluctuation phenomena is very important. Liquid-crystalline supermolecules have an intra-molecular assembly order, inducing heterogeneity in their supramolecular assemblies to produce fluctuations. The orientational fluctuation exists in a nematic phase of liquid crystals. Some frustrated liquid-crystalline phases with a hierarchical structure, such as cybotactic nematic, modulated smectic, and bicontinuous cubic phases, are fascinating fluctuation-induced phases. In addition to these equilibrium phases, a pattern formation that is a nonequilibrium order through fluctuation is one of the most attractive research areas in soft matter. The studies on producing these fluctuation-induced orders in liquid crystals are described. Liquid-crystalline supermolecules in which several mesogens are connected via a flexible spacer have been designed. They have not only a characteristic shape but also an intra-molecular dynamic order. The supermolecules induce the fluctuations in layer structures at a molecular level, producing from the frustrated hierarchical to dynamic dissipative structures. In addition to reviewing molecular design for the hierarchical structures, the pattern propagation in a smectic phase is discussed based on the rotation of smectic blocks through Rayleigh–Bénard convection.

Keywords: liquid crystals; supermolecules; fluctuation, Rayleigh–Bénard convection, phase transition

References

- [1] Wang, Z., Servio, P., Rey, A.D. Structure and pattern formation in biological liquid crystals: Insights from theory and simulation of self-assembly and self-organization. *Front. Soft Matter.* 2022, 2, 904069.
- [2] Nishikawa, H., Sano, K., Kurihara, S., Watanabe, G., Nisjonyanagi, A., Dhara, B., Araoka, F. Nanoclustering mediates phase transitions in a diastereomerically-stabilized ferroelectric nematic system. *Commun. Mater.* 2022, 3, 89

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Advanced phase change materials for thermal energy conversion and storage

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Abstract: Today, energy consumption is a crucial issue with rapid growth. Due to the exhaustion of fossil fuels, energy from renewable energy sources such as the sun, wind, and biomass is needed. The main challenges for further research are the design and manufacture of new advanced materials for efficient energy technologies such as batteries, solar cells, fuel cells, and phase change materials (PCMs) for the storage and conversion of thermal energy. New advanced materials should be fully characterised; in particular, thermal properties, such as phase transition temperature range, phase transition heat and thermal capacity, supercooling, thermal stability, and thermal reliability after multiple heat-cooling cycles, should be detailed studied [1,2]. Phase change materials (PCMs) are important materials for storing thermal energy in the form of latent and sensible heat, which are very important for the efficient use and conservation of waste heat and solar energy. Latent heat storage provides a higher energy storage density and lower temperature differences between heat storage and release than sensible heat storage methods. During the technical development of PCMs, various materials were studied, including inorganic systems (salts, salt hydrates), organic compounds (paraffins or fatty acids), and polymers, such as poly(ethylene glycol). Historically, the relationship between the structure and energy storage characteristics of different materials, including composites, has been studied to understand and improve the heat accumulation/emission mechanisms governing the energy storage characteristics. This work presents the current state of the art of PCMs for thermal energy storage and conversion applications and gives a brief overview of recent efforts to develop new PCMs with improved performance and safety. Special attention is paid to improving thermal conductivity, encapsulation, and shape stabilization with the use of selected nanoadditives.

Keywords: thermal energy, energy storage, phase change materials

References

- [1] Pielichowska, K., Pielichowski, K. Phase change materials for thermal energy storage, *Progress in Materials Science*. 2014, 65, 67-123.
- [2] Pielichowska, K., Pielichowski, K. *Thermal analysis of polymeric materials: methods and developments*, *WILEY-VCH*. 2022, 533-559

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Assessment of extracellular particles and liposomes by interferometric light microscopy

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Abstract: Membrane-enclosed, sub-micron-sized cellular fragments called extracellular particles have become a subject of increasing interest, as they can mediate interactions between cells and serve as drug delivery systems. Extracellular particles are pinched off from cells at the last stage of membrane budding. Once released, they become free to travel with bodily fluids and can be taken up by recipient cells.

Extracellular particles carry proteins, signalling molecules, and nucleic acids or their fragments, which may affect biological activities in the recipient cells. They are considered potential diagnostic and therapeutic vectors, and the development of methods for their harvesting and characterization is highly warranted. However, this presents a challenge, as evidence indicates that processing can significantly influence the identity, number density, size, and composition of EPs in samples.

Interferometric Light Microscopy (ILM) is a recently developed technique that detects particles sized between 80nm and 500 nm. It allows for the presence of a certain level of larger particles and therefore requires minimal sample processing prior to measurement. By analysing interference patterns of incident and scattered light, and assuming that the nanoparticles undergo Brownian motion, the hydrodynamic parameter D_h of the particles and their number density n can be determined. We will report on measurements of D_h and n by ILM in plasma, blood, conditioned media of microalgae, and suspensions of liposomes.

Keywords: Interferometric Light Microscopy, liposomes, extracellular particles, hydrodynamic parameter

References

- [1] Romolo, A., Jan, Z., Zavec, A. B., Kisovec, M., Arrigler, V., Spasovski, V., Podobnik, M., Iglič, A., Pocsfalvi, G., Kogej, K., Kralj-Iglič V. Assessment of Small Cellular Particles from Four Different Natural Sources and Liposomes by Interferometric Light Microscopy *Int. J. Mol. Sci.* 2022, 23(24), 15801 <https://doi.org/10.3390/ijms232415801>
- [2] Berry M, Arko M, Romolo A, Brložnik M, Mrvar Brečko A, Korenjak B, Iglič A, Kadunc Kos V, Kruljc P, Nemec Svete A, Erjavec V, Kralj-Iglič V. Validation of Interferometric Light Microscopy for Assessment of Extracellular Particles in Diluted Plasma: Preparing the Path for Future Clinical Practices. *Proceedings of Socratic Lectures*. 2024, 10, 54-58. <https://doi.org/10.55295/PSL.2024.19>

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Colloidal Soft Matter Physics

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Abstract: Colloidal suspensions are many-body systems composed of tiny particles (ranging in size from a few nanometers to a few microns), usually called colloids, dispersed in a continuous medium typically known as a solvent. From a scientific point of view, colloids serve as model systems to understand, for example, both equilibrium phase behavior (e.g., gas, liquid, solid) and nonequilibrium states of matter (e.g., gels and glasses), the effective interactions in many-body systems, and the mechanical response of materials, which can then also be considered as analogues to atomic, molecular, metallic and biological systems. Furthermore, colloids constitute

an essential part of life; for example, most processes in the human body take place or originate in colloidal suspensions. Furthermore, colloids have an important relevance in many industrial and technological applications, such as paints, foods, medicines, just to mention a few examples. Colloids are used as model systems mainly due to the following characteristics: 1) Colloids and other macromolecules share similar length scales (10 nm - 1 μ m), making them 'visible' and, as a consequence, relatively slow (typical time scales \sim 1 μ s - 1 s), which opens the possibility of following colloidal dynamics and transport processes in real time, 2) interactions between colloidal particles, of the order of thermal energy, also describe the interaction between macromolecules immersed in an aqueous environment and can be "tuned" over a wide range of length scales, 3) since colloidal interactions are relatively weak, they are highly susceptible to external forces and, therefore, their static and dynamic properties can be controlled by the application of external fields, and 4) colloidal suspensions can be studied at the single particle level through different complementary techniques, that is, experiments, computer simulations and theoretical approaches. Therefore, understanding the physical properties of colloidal suspensions allows us to give a qualitative and often quantitative description of soft materials, but also has important implications in Condensed Matter, Chemistry, Materials Science and Engineering, Biology and Biotechnology, among other areas of science.

Colloidal systems open the possibility of exploring a great diversity of phenomena, such as directed self assembly and the formation of structures, as well as the response to external fields, they also serve to answer fundamental questions within the Statistical Physics of Non-Equilibrium States, to attack problems in the context of Biophysics and to facilitate the quantitative prediction of physical properties important for the design, manufacturing, processing of commercial products, that is, technological innovation based on colloidal soft matter. In this talk, I will talk about all these characteristics that make Colloidal Soft Matter Physics a multidisciplinary field, this being, perhaps, one of the new paradigms of contemporary science.

Keywords: soft matter, statistical thermodynamics

References

- [1] Castañeda-Priego, R. Colloidal Soft Matter Physics. *Revista Mexicana de Física*. 2021, 67(5), 1-18. doi: 10.31349/RevMexFis.67.050101
- [2] Herrera-Velarde, S., Euán-Díaz, E. C., Castañeda-Priego, R. Ordering and Dynamics of Interacting Colloidal Particles under Soft Confinement. *Colloids Interfaces*. 2021, 5(2), 29 doi: 10.3390/colloids5020029.
- [3] Gallegos, J. A.; Perdomo-Pérez, R.; Valadez-Pérez, N. E.; Castañeda-Priego, R. Location of the gel-like boundary in patchy colloidal dispersions: Rigidity percolation, structure, and particle dynamics. *Phys. Rev. E*. 2021, 104, 064606 doi:10.1103/PhysRevE.104.064606

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Revisiting the role of ions in advanced liquid crystal materials

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Abstract: Modern applications of molecular liquid crystals continue to expand at a breathtaking pace. Liquid crystals are at the heart of various advanced displays, smart windows, reconfigurable meta-surfaces, microwave elements for communication and space exploration, spatial light modulators, miniature tunable lasers, lenses, filters, transducers, and sensors, to name a few. As a rule, new applications require new geometries, novel mesogenic materials, or unusual combinations of existing ones. Because ions can impact the response of molecular liquid crystals to external electric fields and affect the power consumption and overall performance of liquid crystal devices, it is important to study ions and their effects in such systems. The goal of this lecture is to provide a coherent and informative overview of ions in molecular liquid crystals, with an emphasis on overlooked and new ionic phenomena in such materials. The lecture also highlights existing challenges in ionic measurements, various sources of ion generation, and new methods for controlling ions in molecular liquid crystals. Implications of ionic effects for both liquid crystal science and technology, as well as future research directions, complete the lecture.

Keywords: liquid crystals, mesogenic materials, ion measurement techniques

References

- [1] Garbovskiy, Y. Evaluating the Concentration of Ions in Liquid Crystal Cells: Hidden Factors and Useful Techniques. In *Proceedings of the 2nd International Online Conference on Crystals*, 2020; 1-8
- [2] Garbovskiy, Y. Time-dependent electrical properties of liquid crystal cells: Unravelling the origin of ion generation. *Liq. Cryst.* 2018, 45, 1540–1548, doi:10.1080/02678292.2018.1455228
- [3] Garbovskiy, Y. Nanoparticle-enabled ion trapping and ion generation in liquid crystals. *Adv. Condens. Matter Phys.* 2018, 2018, 1–8, doi:10.1155/2018/8914891

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Critical fluctuations: The case of pretransitional effects in the liquid phase of liquid crystals and plastic crystals forming materials

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Abstract: Colloids based on liquid crystals with a small addition of nanoparticles are considered promising systems for applications ranging from the new generation of displays and photonics devices to photovoltaic panels. They also constitute a new category of soft matter systems, with unique properties well beyond those expected from their constituents. It is surprising that, despite extensive research, the impact of pretransitional fluctuations on the properties detected remains poorly understood. This contribution presents experimental evidence for selected rod-like compounds, such as 5CB, 12CB, and MBBA, in combination with BaTiO₃ nanoparticles. Particularly worth stressing is the decisive impact of pretransitional fluctuations in the isotropic liquid phase, which extend to at least 50K above the clearing temperature and span the entire liquid-crystalline mesophase. Significant for applications is finding the permanent ordering of the nematic phase by adding a small amount of nanoparticles, i.e., solely endogenic, and avoiding strong external fields (electric, magnetic) or by covering the capacitor plates with ordering-supportive polymeric nanolayers. For fundamentals, the discovery of a discontinuous isotropic–nematic transition under the simultaneous influence of pressure and a small amount of nanoparticles is essentially significant.

Keywords: pretransitional fluctuations, nanoparticles, plastic crystals

References:

- [1] Łoś, J., Drozd-Rzoska, A., Rzoska, S. J., Starzonek, S., Czupryński, K., Mukherjee, P. Near-continuous isotropic–nematic transition in compressed rod-like liquid crystal-based nanocolloid, *Journal of Molecular Liquids* **382**. 2023, 121884, <https://doi.org/10.1016/j.molliq.2023.121844>
- [2] Łoś, J., Drozd-Rzoska, A., Rzoska, S. J. Critical-like behaviour of low-frequency dielectric properties in compressed liquid crystalline octyloxycyanobiphenyl (8OCB) and its nanocolloid with paraelectric BaTiO₃. *Journal of Molecular Liquids* **377(4)**. 2023, 121555. doi:10.1016/j.molliq.2023.121555
- [3] Drozd-Rzoska, A., Łoś, J., Rzoska, S.J. The dominance of pretransitional effects in the liquid crystal based nanocolloids: nematogenic MBBA with the transverse permanent dipole moment and BaTiO₃ nanoparticles. *Nanomaterials* **14**. 2024. 655. <https://doi.org/10.3390/nano14080655>

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Linear and non-linear dielectric properties of reverse micelles

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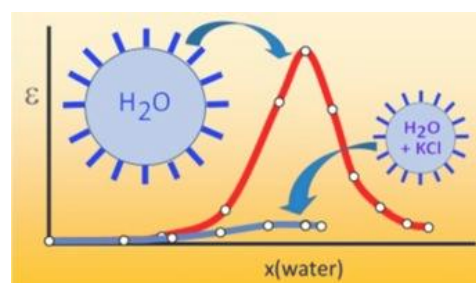
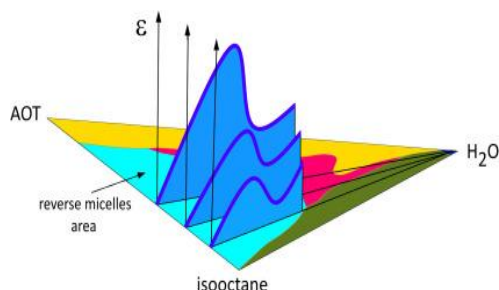
Abstract: Reverse micelles (RMs) are self-assembled structures that form in ternary (or more complex) mixtures composed of a nonpolar phase, a polar phase, and a surfactant—sometimes accompanied by a co-surfactant. The characteristics of RMs can be tuned or modified through the incorporation of various additives.

The lecture will present and discuss the intriguing dielectric properties of reverse micelles formed in three-component systems water + oil + surfactant. Reverse micelles are nanoparticle aggregates consisting of an aqueous core, a surfactant shell, and non-polar solvent (oil). The first experiments conducted in our laboratory have already demonstrated the possibility of measuring the nonlinear dielectric effect (NDE), even though the system is formally a mixture of water, ionic salt. This was an astonishing result, but under normal conditions, a mixture of water and ionic salt is difficult to measure using the NDE technique. The NDE effect was found to be positive and extremely large compared to simple dipolar liquids, including water, where the NDE effect is large enough. These experiments inspired us to further investigate the dielectric properties of reverse micelles. The lecture will present our results obtained in water + isooctane + AOT systems and in systems doped with ionic salts. These data have been published before, but I hope to present some interesting, new data.

Keywords: nonlinear dielectric effect, reverse micelles, dipolar liquids

References

- [1] Małycha, K., Orzechowski, K., Burakowski, A. Influence of the presence of ions on the dielectric properties of reverse micelle systems. *Journal of Molecular Structure*. 2024, 1318, 139370/1-139370/5. doi: 10.1016/j.molstruc.2024.139370
- [2] Małycha, K., Burakowski, A., Gliński, J., Hongyu, N., Shulin, B., Orzechowski, K. Characterization of isooctane/AOT/ water reverse micelles by dielectric spectroscopy, dynamic light scattering and acoustic methods. *Journal of Molecular Liquids*. 2021, 330, 115335/1-115335/8. doi: 10.1016/j.molliq.2021.115335
- [3] Małycha, K., Pocheć, M., Orzechowski, K. Non-linear dielectric effect in reverse micelles system. *Journal of Molecular Liquids*. 2019, 291, 111344/1-4. doi: 10.1016/j.molliq.2019.111344



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Enzyme organization and maximum entropy production principle

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Abstract: We intend to present a theoretical study of the intermediate-metabolite driven first-order phase transition between two qualitatively different forms of enzyme organization. We consider transition between enzyme cascade assembled by two soluble enzymes and corresponding enzymatic complex or so-called metabolon. Both forms of enzyme organizations are of basic importance in catalysis of multi-step biochemical reactions in biological cells and cell signalling. The above-mentioned distinct types of enzymatic organizations are investigated theoretically by using the Maximum Entropy Production Principle as a general theoretical framework. We demonstrate that MEPP is of central importance for thermodynamic selection and description of catalytically optimal steady states in biological reactions and show that optimization of the entropy production rate in a complex multi-step enzymatic process leads spontaneously also to maximal Shannon Information Entropy, fingerprinting the statistically most probable steady state of an open non-equilibrium reaction system. The notion of metabolons is very advanced in plant metabolism. Experimental observation of metabolons is very formidable task, since interactions involved in this level of enzyme organization are of transient character and ephemeral in nature. This seems to be one of the main reasons why the essence of the underlying mechanism of the spatial and temporal (re)organization of soluble enzymes into multi-enzyme complexes remains elusive and not well understood. Formation of multi-enzyme complexes is, very plausible, explained as protein liquid-liquid phase separation. The difficulties with experimental observations of metabolons and their spontaneous formation in living cells gives a lot of space to study this phenomenon with theoretical models. By combining various theoretical approaches such as MEPP, Shannon information entropy, kinetic modelling, stability analysis, and metabolic control analysis, we demonstrate that enzyme cascade to enzyme complex transformation is triggered by asymmetry between the probabilities of enzymatic functional states in enzyme cascade. A detailed analysis clearly reveals that such transformation shows characteristics of first-order phase transition. We illustrate that steady states could be efficiently described by the universal Maximum Entropy Production mechanism, and the resulting states at the same time exhibit maximal Shannon information entropy. Furthermore, the transition between competing enzyme organizations could be described as a first-order phase transition described by an adequate order parameter.

Keywords: theoretical modeling, irreversible thermodynamics, Shannon information entropy, first-order phase transition, enzyme organization

References

- [1] Schoffelen, S., van Hest J. C. M. Multi-enzyme systems: bringing enzymes together in vitro. *Soft Matter*. 2012, 8, 1736-1746. doi: 10.1039/c1sm06452e
- [2] Pröschel, M., Detsch R., A. R. Boccaccini, A. R., Sonnewald, U. Engineering of Metabolic Pathways by Artificial Enzyme Channels. *Front. Bioeng. Biotechnol.* 2015, 3, 1-13. doi: 10.3389/fbioe.2015.00168

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Experimental investigations of soft- and bio-matter: From ferroelectric nematic liquid crystals to biomimetic membranes

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Abstract: A few examples of experimental investigations in soft and biomatter are discussed. Thanks to high-resolution calorimetry, we can get precise and detailed information about phase transitions in liquid crystals. High resolution, Peltier element-based adiabatic scanning calorimetry (PASC) and quartz crystal microbalance with dissipation monitoring (QCMD) have been employed to study ferroelectric nematic liquid crystals and biomimetic membranes, respectively. New types of ferroelectric nematic liquid crystal compounds, referred to as mixtures with 4-[(4-nitrophenoxy)carbonyl]phenyl 2,4-dimethoxybenzoate (RM734). RM734 and compound 2,3',4',5'-tetrafluoro[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate (DIO), have been studied by means of PASC. We report on the critical behavior of phase transitions between the classical nematic, intermediate, and ferroelectric nematic phases. An intermediate phase, occurring between the nematic and ferroelectric nematic ones, is evidenced by PASC for the first time in the case of RM734. Finally, the amended phase diagram of RM734 and DIO mixtures is presented. In the case of biomimetic membranes, QCMD has been employed to assess the quality of solid supported lipid bilayers formed by the solvent-exchange method under different experimental conditions. The individual roles of the solid surface, the aqueous (buffer) medium, and the lipid phase are addressed. In addition, we briefly discuss how QCMD can be utilized to study the interactions between solid-supported lipid membranes and nanoparticles.

Keywords: soft matter, biomatter, nematic liquid crystals

References

- [1] Thoen, J., Cordoyiannis, G., Jiang, W., Mehl, G. H., Glorieux, C. Phase transitions study of the liquid crystal DIO with a ferroelectric nematic, a nematic, and an intermediate phase and of mixtures with the ferroelectric nematic compound RM734 by adiabatic scanning calorimetry. *Physical Review E*. 2023. **107**. doi: 10.1103/PhysRevE.107.014701.
- [2] Thoen, J.; Cordoyiannis, G., Korblova, E., Walba, D. M., Clark, N. A., Jiang, W., Mehl, G. H., Glorieux, C. Calorimetric evidence for the existence of an intermediate phase between the ferroelectric nematic phase and the nematic phase in the liquid crystal RM734. *Physical Review E*. 2024, **110**. doi: 10.1103/PhysRevE.110.014703.
- [3] Cordoyiannis, G., Losada-Pérez, P., Bar, L. Recent advances in quartz crystal microbalance with dissipation monitoring: Phase transitions as descriptors for specific lipid membrane studies. *Advances in Biomembranes and Lipid Self-Assembly*. 2021, 107–128. doi: 10.1016/bs.abl.2021.11.004.
- [4] Bibissidis, N., Betlem, K., Cordoyiannis, G., Prista-von Bonhorst, F., Goole, J., Raval, J., Daniel, M., Gózdź, W., Iglič, A., Losada-Pérez P. Correlation between adhesion strength and phase behaviour in solid-supported lipid membranes. *Journal of Molecular Liquids*. 2020, 320. doi: 10.1016/j.molliq.2020.114492

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On the role of orientational and lateral distribution of membrane attached I-BAR proteins and actin forces in the shape and migration of cells

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Abstract: Protrusions at the leading-edge of a cell play an important role in cellular spreading and motility. However, the physics of cell mobility is still not well understood. We present a combined theoretical and experimental study of the cell movement on the surface of different geometry as well as the mechanism of efficient phagocytosis and the mechanism of coiling of cellular protrusions around fibers. Our theoretical model describes the membrane leading-edge that is produced by curved membrane proteins that recruit the protrusive forces of actin polymerization, and identifies the role of bending and adhesion energies. Among other our model recovers the observed cell migration on the sinusoidal substrate, where cells move along the grooves (minima), while avoiding motion along the ridges. Further we predicted in accordance with experimental results that the cell's leading-edge may coil on fibres with circular cross-section (above some critical radius), but the coiling ceases for flattened fibres of highly elliptical cross-section. We also considered the phagocytosis of spherical and non-spherical particles and found that non-spherical particles are more difficult to engulf in comparison to the spherical particles of the same surface area. For non-spherical particles, the engulfment time crucially depends on the initial orientation of the particles with respect to the vesicle. Our model also offers a mechanism for the spontaneous self-organization of the actin cytoskeleton at the phagocytic cup, in good agreement with recent high-resolution experimental observations.

Keywords: minimal cell, skeleton, BAR domains, spherical and non-spherical particles

References:

- [1] Sadhu, R.K., Hernandez-Padilla, C., Eisenbach, Y.E., Penič, S., Zhang, L., Vishwasrao, H.D., Behkam, B., Konstantopoulos, K., Shroff, H., Iglič, A., Peles, E., Nain, A.S., Gov, N.S. Experimental and theoretical model for the origin of coiling of cellular protrusions around fibers. *Nature Communications* 14. 2023, 5612. doi: 10.1038/s41467-023-41273-y.
- [2] Sadhu, R.K., Barger, S. R., Penič, S., Iglič, A., Krendel, M., Gauthiere, N.C., Gov, N.S. A theoretical model of efficient phagocytosis driven by curved membrane proteins and active cytoskeleton forces. *Soft Matter*. 2023, 19, 31-43. doi: 10.1039/D2SM01152B
- [3] Mesarec, L., Gózdź, W., Kralj-Iglič, V., Kralj, S., Iglič, A. Coupling of nematic in-plane orientational ordering and equilibrium shapes of closed flexible nematic shells. *Scientific Reports*. 2023, 13. doi: 10.1038/s41598-023-37664-2

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On the liquid crystal ordering of nucleic acids and its intimate connection to Watson-Crick pairing

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Abstract: One prominent theory concerning the origins of life is the “RNA world” hypothesis, proposing that ribonucleic acid (RNA) was the first bio–macromolecule to emerge in the prebiotic world due to its combined ability to store genetic information and catalyze chemical reactions, including its own synthesis. However, one of the primary concerns with this hypothesis is the lack of a highly efficient, prebiotically compatible mechanism capable of explaining the formation of RNA chains from simple nucleotides.

During this lecture, three findings will be presented that suggest a central role of molecular self-assembly in facilitating prebiotic RNA formation and stability.

The transfer and memory of genetic information relies on Watson-Crick selective base pairing of DNA and RNA chains, universally considered a defining characteristic of these polymers. We found that Watson-Crick selectivity is present even in the absence of the polymeric backbone. Concentrated aqueous solutions of mononucleotides triphosphates and of cyclic mononucleotide monophosphates develop chromonic liquid crystal phases that involve the formation of Watson-Crick pairs. This behavior is remarkable since the release of the constraints provided by the phosphodiester side chain of the mononucleotides could enable a plethora of non-Watson-Crick pairing, including any alternation of parallel and antiparallel base pairing. We in particular studied the reactivity and self-assembly abilities of prebiotically compatible 2'-3' cyclic nucleosides monophosphates during drying at various pH levels. We observed, while drying at room temperature, the formation of liquid crystalline phases and birefringent aggregates in solutions of individual nucleotides and mixtures. When such samples are cyclically dried and hydrated in basic environments, nucleotides spontaneously oligomerize with a reactivity peak around pH 10, resulting in polymerization yields up to 70%. This behavior suggests an important templating role of liquid crystal and/or crystalline self-assembled structures. Liquid crystal ordering of DNA and RNA oligomers has a significant effect on their chemical binding. When the oligomers are equipped with reactive terminals, the onset of molecular ordering boosts the efficiency of their chemical ligation into long linear chains, a process in which the broken symmetry involved in the self-assembly has the key role of preventing the formation of short circular chains, which would otherwise dominate. The combination of these results suggests that NTP could spontaneously polymerize when prompted by their liquid crystal ordering, a topic of our current research activity. If this were true, DNA and RNA chain would emerge as a bona fide “self-synthesizing material”, i. e. a system that catalyzes the formation of molecules that stabilize their own self-assembly.

Keywords: Watson-Crick pairing, liquid crystals, nucleic acids

References

- [1] Tony Z Jia, T.Z., Bellini, T., Clark, N., P. Fraccia, T.P. A Liquid Crystal World for the origins of life. *Emerg Top Life Sci.* 2022, 6(6), 557-569. doi: 10.1042/ETLS20220081
- [2] Todisco, M., Fraccia, T. P., Greg P. Smith, G.P., Corno, A., Bethge, L., Klusmann, S., Paraboschi, E.M., Asselta, Diego Colombo, D., Zanchetta, G., Clark, N. A., Bellini, T. Nonenzymatic polymerization into long linear RNA templated by liquid crystal self-assembly. *ACS Nano*, 2018, doi: 10.1021/acsnano.8b05821

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Topological defects as detectors for nanoparticles

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Abstract: Topological defects (TDs) are an unavoidable consequence of continuous symmetry-breaking phase transitions. They appear at all scales of physical systems, including particle physics, condensed matter and cosmology. Due to their topological origin, they display several universalities that are independent of the systems' microscopic details. For example, they might even explain the stability of “fundamental particles” via topological protection if fields represent a fundamental entity of nature. Furthermore, by invoking curvature inhomogeneities in spacetime, they could explain the nature of “dark matter” and “dark energy”.

It is of interest to find a system where TDs are relatively easily accessible. For this purpose, liquid crystal (LC) phases represent an ideal testing ground owing to their extraordinary and unique combination of optical anisotropy, fluidity, and softness. Furthermore, they possess a rich variety of different phases and configurations that contain practically all qualitatively different TDs from a symmetry perspective. Consequently, LCs could be exploited as a convenient window into the fundamental behavior of TDs. In addition, TDs in LCs could be employed in diverse electro-optical applications.

In this presentation, I present studies of diverse thermodynamically stable controllable assemblies of TDs in orientationally ordered LC films in bulk and flexible, closed, curved surfaces. Topological defects are in general energetically costly, and systems avoid them. We will focus on conditions where trapping of appropriate nanoparticles in the cores of topological defects could stabilize different assemblies of TDs. Because formation of TDs has big impact at mesoscopic scale such events are relatively easily observed, for example, using optic microscopy. We will demonstrate that such system could be efficiently exploited for sensitive detection of specific nanoparticles.

Keywords: topological defects, mesoscopic scale, nanoparticles

References

- [1] Pišljari, J., Ghosh, S. Turlapati, S., Rao, N., V., S., Škarabot, M., Mertelj, A., Petelin, A., Nych, A., Marinčič, M., Pusovnik, A., Ravnik, M., and Muševič, I. Blue phase III: Topological fluid of skyrmions, *Phys. Rev. X*. 2022, 12, 011003-1 -011003-22. doi: 10.1103/PhysRevX.12.011003
- [2] Repnik, R.; Mathelitsch, L.; Svetec, M.; Kralj, S. Physics of defects in nematic liquid crystals, *European Journal of Physics*, 2003, **24**, 481–492. doi: 10.1088/0143-0807/24/4/366
- [3] Repnik, R.; Niž, V. P.; Kralj, S. Mixtures of Nanoparticles and Liquid Crystal Phases Exhibiting Topological Defects, *Molecular Crystals and Liquid Crystals*. 2012. 560(1), 115–122. DOI:10.1080/15421406.2012.663187

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Glass Still Breaks

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Abstract: Oxide glasses represent one of the most significant families of engineering and functional materials due to their highly tunable physical properties. Nevertheless, their inherent brittleness remains a major limitation, greatly constraining their practical applications. Although notable advances have been achieved in this field, a true breakthrough toward creating ultra-damage-resistant and ductile oxide glasses has yet to be realized. Oxide glasses with improved damage and fracture resistance are critically needed. Traditionally, new glass compositions have been developed through time-consuming trial-and-error experimentation. To enable a bottom-up design of new compositions and microstructures, an improved understanding of the variations in mechanical properties at the atomic level is needed. In turn, this builds on knowledge of the structural deformation mechanisms of the glasses under high local stress. In this talk, I will discuss our progress in achieving this understanding through atomistic simulations, high-pressure studies, and structural characterization based on NMR spectroscopy, x-ray, and neutron total scattering experiments. The focus is on how structural variations at both the short-range length scale (e. g. coordination numbers) and medium-range length scale (e. g. ring structures) affect the hardness, crack initiation resistance, and fracture toughness of different families of oxide glasses. I will also discuss our recent progress in in-situ mechanical characterization.

Keywords: oxide glasses, structural deformation

References

- [1] Januchta, K., Stepniewska, M., Jensen, L. R., Zhang, Y., Somers, M. A. J., Bauchy, M., Yue, Y., & Smedskjær, M. M. Breaking the limit of micro-ductility in oxide glasses. *Advanced Science*, 2019. 6(18), Article 1901281 – 1-9 doi:10.1002/advs.201901281
- [2] Kirchner, K. A., Cassar, D. R., Zanutto, E. D., Ono, M., Kim, S. H., Doss, K., Bødker, M. L., Smedskjær, M. M., Kohara, S., Tang, L., Bauchy, M., Wilkinson, C. J., Yang, Y., Welch, R. S., Mancini, M. & Mauro, J. C. Beyond the average: spatial and temporal fluctuations in oxide glass-forming systems. *Chemical Reviews*. 2023. 123, 4, 1774–1840. doi: 10.1021/acs.chemrev.1c00974

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Reaching low-energy states via non-conventional pathways: predicting nonequilibrium kinetics via the SAP

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Abstract: The properties of an ensemble of objects at thermodynamic equilibrium do not change with time. Experience tells us, however, that such observation is rarely encountered in nature. The transformation of buds into flowers and then fruits, the rearrangements of plates on the surface of planets, and even the whole human body over its lifetime are just a few, among the many, examples of systems far from thermodynamic equilibrium. At the molecular level, equilibration kinetics –the time evolution of a system’s properties toward a less energetic state– are intimately coupled to molecular motion. In line with Onsager’s regression hypothesis, the macroscopic relaxation of a nonequilibrium system (dissipation) obeys the same laws of molecular dynamics in equilibrium conditions (spontaneous microscopic fluctuations). In the case of liquids, equilibration is usually driven by the so-called α -modes, which are responsible for density fluctuations and require time scales that quickly diverge upon cooling. Growing experimental evidence indicates, however, the presence of a different, alternative pathway of weaker temperature dependence. Such equilibration processes exhibit a temperature-invariant activation barrier, on the order of 100 kJ mol⁻¹. We have recently identified the underlying molecular process responsible for this class of Arrhenius equilibration mechanisms with a slow mode (SAP), universally observed in the dynamics of polymers and small molecules. The SAP, which we show is intimately connected to high-temperature rheological behavior, can efficiently drive melts and glasses toward more stable, less energetic states. Based on the experimental findings collected so far on polymers and small molecules, we present a new framework for the equilibration of materials considering the contributions of both the SAP and the α -modes. In support of its potential, we demonstrate that our model is capable of providing quantitative predictions on the adsorption rate of polymers, a key parameter for the performance and durability of ultrathin polymer films.

Keywords: SAP, thermodynamic, nonequilibrium system

References

- [1] Onsager, L. Reciprocal relations In Irreversible Processes. I. *Physical Review*. 1931, 37(4), 405-426. doi: <https://doi.org/10.1103/PhysRev.37.405>
- [2] Chandran, S., Reiter, G. Segmental rearrangements relax stresses in nonequibrated polymer films. *ACS Macro Lett.* 2019, 8(6), 646-650. doi: 10.1021/acsmacrolett.9b00116. Epub 2019 May 23
- [3] Caporaletti, F., Napolitano, S. The slow Arrhenius process in small organic molecules. *Phys. Chem. Chem. Phys.* 2024, 26, 745-748. <https://doi.org/10.1039/D3CP05044K>

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Liquids and Glass Transition: a general problem of dynamical arrest in Soft Matter

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Abstract: The viscosity of liquids that can be supercooled below the first-order freezing transition increases dramatically as the temperature decreases. At a certain temperature, known as the glass transition temperature (T_g), the viscosity becomes so high that liquid-like flow becomes too slow to measure. Below T_g , the material is referred to as a glass or amorphous solid. This phenomenon, which simultaneously involves thermodynamics, dynamics, and structure, is of ongoing and likely future interest across various areas of Soft Matter. Investigating it requires the use of multiple techniques across a wide range of length and time scales. One compelling hypothesis is that the strong temperature dependence of the dynamics, regardless of molecular specifics, may be due to collective or cooperative behavior, characterized by a growing length scale that extends from slightly above the melting temperature deep into the supercooled regime. However, a more complete description of the rich phenomenology associated with glass formation and its final properties often requires correlations to be drawn, particularly between the so-called fragility just above T_g and the properties of the glass just below it. Among the various pathways to forming a glass, this study will focus on the effects of pressure (i.e., density), temperature, and nanoscale confinement.

Keywords: glass transition, soft matter, first-order transition

References

- [1] Tarjus, G., Kivelson, D., Mossa, S., Alba-Simionesco, C. Disentangling density and temperature effects in the viscous slowing down of glassforming liquids. *J. Chem. Phys.* 2004, 120, 6135–6141. doi: 10.1063/1.1652784
- [2] Cailliaux, A., Alba-Simionesco, C., Frick, B., Willner, L., Goncharenko, I.. Local structure and glass transition of polybutadiene up to 4 GPa. *Phys. Rev. E.* 2003, 67(1 Pt 1). doi: <https://doi.org/10.1103/PhysRevE.67.010802>
- [3] Alba-Simionesco, C. Organic glass-forming liquids and the concept of fragility. *Comptes Rendus Physique.* 2023, 24(S1), 177–198 doi: 10.5802/crphys.148

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The new paradigm for the pressure-related previtreous evolution of the primary relaxation time and related properties

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Abstract: If the cooling rate is rapid enough, it is possible to bypass a discontinuous liquid-solid crystal transition and to reach the solidification from the supercooled liquid state to the amorphous, solid glass after reaching the glass temperature (T_g). However, for many materials, the glass state can be reached at almost any cooling rate. Temperature changes are related to the evolution of the activation energy, but the glass state can also be reached by compression, which influences the activation volume and intermolecular distances solely. In this case, the glass state is reached when passing the vitrification (glass) pressure P_g . The impact of both temperature and pressure studies create the $T_g(P)$ or $T_g(P_g)$ line, which separates the aforementioned states.

The previtreous domain extends 100 K above T_g and several hundreds MPa below P_g . This region exhibits unique properties, which hallmark constitute non-Arrhenius type, long-range changes of dynamic properties. For decades, the description of such pressure-dependent changes in relaxation time (τ) or viscosity (η) has been based on exponential relations that parallel the VFT equation used in temperature studies. However, such approaches effectively reproduce experimental data. This contribution recalls model-derivation proposed recently in refs. showing that fundamentally justified by the nature of the experimental data follows the critical-like type, namely: $\tau(P), \eta(P) \propto (P^+ - P)^{-\varphi}$. It results from $d \ln [\tau(P), \eta(P)] / dP \propto \varphi / (P^+ - P)$ universal changes, for a property proportional to the activation volume. The latter estimates the singular pressure and the power exponent, so the nonlinear fitting of $\tau(P)$ can be avoided, which essentially improves and supports the reliability of the analysis in the ultraviscous/ ultraslow domain. Further, it leads to the new, fundamentally coherent, universalistic plot linking changes of dynamical properties in the previtreous domain.

Keywords: vitrification, previtreous domain, glass-forming liquids

References

- [1] Drozd-Rzoska, A.; Rzoska, S. J.; Starzonek, S. *New scaling paradigm for dynamics in glass-forming systems. Progress in Materials Science.* 2023, 134, 101074. <https://doi.org/10.1016/j.pmatsci.2023.101074>
- [2] Drozd-Rzoska, A. *Universal behavior of the apparent fragility in ultraslow glass forming systems. Scientific Reports* 9. 2019, 6816. doi:10.1038/s41598-019-42927-y
- [3] Drozd-Rzoska, A. *Activation volume in superpressed glass-formers. Scientific Reports* 9(1). 2019, 1-9. doi:10.1038/s41598-019-49848-w
- [4] Drozd-Rzoska, A. *Pressure-related universal previtreous behavior of the structural relaxation time and apparent fragility. Front. Mater.* 6, 2019, 103, doi: 10.3389/fmats.2019.00103

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Young Scientist Lectures

♠ Aleksander Szpakiewicz-Szatan — Poland

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♠ Izabela Łukaszewska — Poland

♠ Joanna Łoś — Poland

♠ Maha Zid — Slovenia

♠ Melani Potrč — Slovenia

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High pressure treatment of sodium olivine-like glass: Possible future cathode material

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Abstract: High-pressure treatment is one of the least examined fields in the physics of energy storage materials. Today, most of the batteries used are based on various lithium-based. One of the more promising lithium combinations is lithium phosphoolivine (LiFePO₄) due to its safety and use of common (besides lithium) elements. However, the most significant drawback of this compound (besides lithium scarcity) is its moderate conductivity, which can be improved by carbon doping. To address those shortcomings, our team studied the impact of high-pressure high-temperature treatment on this compound and its sodium-based analog (NaFePO₄).

Heat treatment under pressure ranging from 1 to 3 GPa enabled us to transform amorphous phosphoolivine analogs into nanocrystalline composites embedded in a glassy matrix. High-pressure heat treatment was correlated with in situ high-pressure thermal analysis. Further atmospheric-pressure Broadband Dielectric Spectroscopy and X-Ray Diffraction measurements were used to detect permanent changes in the electrical and structural properties of those materials (within the potential application range).

Obtained nanocomposites exhibit improved electrical properties - apparent DC electric conductivity was increased by orders of magnitude, and apparent activation energy was reduced. It was confirmed that the observed effect was stronger for the sodium analogue than for the lithium. Furthermore, the sodium analogue exhibits different performance in electronic and ionic conductivities depending on temperature and sample state (glassy or nanocomposite), as further supported by AC conductivity studies.

Keywords: high pressure, energy storage

References

- [1] Szpakiewicz-Szatan A., Pietrzak T., Sierakowski K., Boćkowski M., Rzoska S. J., Garbarczyk J., Starzonek S. Nanocrystallization of Bi₂O₃ based system from the glassy state under high compression. *Materialia*. 2024, 33, 1-6. doi: <https://doi.org/10.1016/j.mtl.2023.101975>
- [2] Szpakiewicz-Szatan A., Starzonek S., Pietrzak T., Garbarczyk J., Rzoska S.J., Bockowski M., Novel High-Pressure Nanocomposites for Cathode Materials in Sodium Batteries. *Nanomaterials*. 2023, 13(1), 1-12. doi: <https://doi.org/10.3390/nano13010164>

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Application of waste wool fibres in sustainable controlled-release fertilizers

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Abstract: In recent years, climate change has significantly challenged the agricultural sector. The rising population has escalated food demand, forcing farmers to expand their fields and use more fertilizers. Additionally, the increasing frequency of droughts led to more intensive irrigation of crops. A promising solution to these issues is the use of controlled release fertilizers (CRF), which improve nutrient efficiency and reduce environmental impact. In our studies, the focus was on utilizing wool and biodegradable polymers of natural origin to develop a fertilizer material with a prolonged release time. Waste sheep wool holds a significant potential for agricultural use. This biodegradable and biocompatible natural fibre is rich in keratin, making it an excellent source of nutrients for plants. One of its standout characteristics is its ability to absorb water. This property enhances soil moisture retention, reducing the need for frequent irrigation. In this study, sheep wool from Polish mountain sheep was selected as a main ingredient for a controlled release fertilizer in form of polymer composite. The addition of wool is intended to act as a factor that prolongs water retention in the soil and, as the fibre degrades, to gradually release nitrogen, sulphur, and other nutrients, as well as added fertilizer salts, into the soil. One of the materials used in a study as a matrix are polymer hydrogels, which are being considered in research for modern agricultural solutions as components of fertilizers. They are capable of storing large amounts of water and may help reduce the need for additional irrigation.

The aim of this study was to investigate the ability of wool-loaded hydrogel materials to retain water. To do so, the absorption capacity of the materials and the study of soil water retention in time was conducted. Additionally, characterization of the water in hydrogel composites was carried out using thermal analysis. Preliminary studies have assessed wool as a suitable material for use in fertilizer-like materials. The addition of fibre can improve soil retention capacity and supply nutrients such as nitrogen and sulphur over a longer period. In order to produce hydrogel CRF fertilizers capable of storing water and increasing soil retention, the concentration of the polymer and the cross-linking solution should be adjusted accordingly. In addition, great attention should be paid to the challenge of maintaining the stability and repeatability of wool hydrogel materials compared to other biodegradable polymers considered for matrices.

Keywords: alginates, bioactive compounds, hydrogel materials

References

- [1] Priya, E., Jha, E., Sarkar, S., & Maji, P. K. (2024). A urea-loaded hydrogel comprising cellulose nanofibers and carboxymethyl cellulose: An effective slow-release fertilizer. *Journal of Cleaner Production*, 2024, 434, Article 140215. <https://doi.org/10.1016/j.jclepro.2023.140215>
- [2] Molik, E., Szatkowski, P., Flis, Z., Suchorowiec, K., Szczepanik, E., Niemiec, M., Komorowska, M., & Matusevičius, P. Tradition and innovation in the protection of the natural environment of mountain regions. *Acta Scientiarum Polonorum: Formatio Circumiectus*. 2023. 22(3), 33–40. <https://doi.org/10.15576/ASP.FC/2023.22.3.09>
- [3] Niu, C., Lin, Z., Fu, Q., Xu, Y., Chen, Y., & Lu, L. An eco-friendly versatile superabsorbent hydrogel based on sodium alginate and urea for soil improvement with a synchronous chemical loading strategy. *Carbohydrate Polymers*. 2024, 327, Article 121676. <https://doi.org/10.1016/j.carbpol.2023.121676>

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Tailoring properties of non-isocyanate poly(hydroxyurethanes) by modulating the concentration of hydrogen donor/acceptor groups along the polymer chain

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Abstract: Non-isocyanate poly(hydroxyurethanes) (NIPUs, PHUs) constitute an environmentally friendly class of polyurethanes that are obtained without the use of toxic isocyanates. PHUs are synthesized through aminolysis of cyclic carbonates (CC). The presence of hydroxyl groups in the vicinity of urethane ones strongly influences the properties of PHUs. In comparison to conventional polyurethanes (PU), PHUs tend to exhibit lower crystallinity, enhanced chemical resistance and adhesiveness, and increased absorption of water and vapor. The properties of PHUs can be tailored by the proper selection of amines and cyclic carbonates. Modulating chain length and structure, rigidity, and functionality of CCs and amines influence thermal and mechanical properties of final materials. Here, we present results of our studies on the possibility of tailoring PHU mechanical, thermal, and hydration properties by modulating the number of secondary amino groups along the main chain. PHUs are synthesized via aminolysis of poly(propylene oxide) based cyclic carbonate (PPO-CC). The content of secondary amino groups is modulated by different mass ratios of 1,4-diaminobutane (DAB) and triethylenetetraamine (TETA) in the amine component. Changes in hydrogen bonding density as a function of TETA content were studied using Fourier transform infrared spectroscopy (FTIR). It was shown that increasing TETA content increases hydrogen bonding density, with the exception of the pure DAB composition. The changes in mechanical properties correlate with changes in hydrogen bonding density: materials with lower hydrogen bonding densities exhibit compromised shape stability, while materials with a denser hydrogen bond network constitute durable elastomers. Hydrogen bonding in PHUs also determines their glass transition temperature, as was observed by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and dielectric relaxation spectroscopy (DRS). Introducing secondary amino groups into the PHU chain also allows for tailoring the water sorption. Water vapor sorption isotherms were recorded in the relative humidity range 0-97%. It was shown that while hydroxyurethane groups constitute the primary hydration sites, secondary amino groups act as secondary hydration sites, modulating monolayer capacity and vapor sorption. The changes in molecular mobility of the studied systems upon water sorption were monitored by DSC and discussed with regard to changes in morphology observed by FTIR. Three regions of the decrease in glass transition temperature were distinguished and attributed to the following three mechanisms: initial scission of hydrogen bonds, plasticization, and slaving.

Keywords: donor group, acceptor group, glass transition

References

- [1] Cornille, A., Auvergne, R., Figovsky, O., Boutevin, B., & Caillol, S. A perspective approach to sustainable routes for non-isocyanate polyurethanes. 2017. *European Polymer Journal*. 2017, 87, 535-552. <https://doi.org/10.1016/j.eurpolymj.2016.11.027>

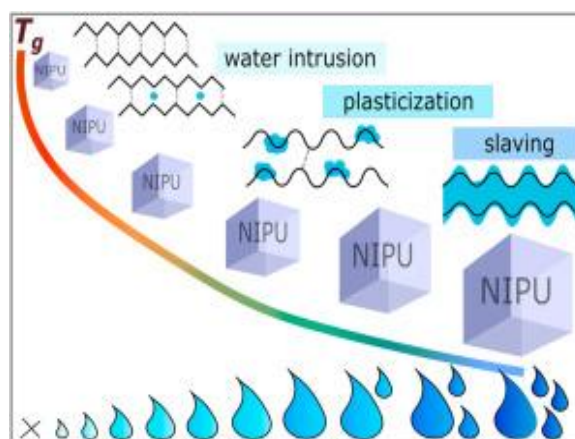
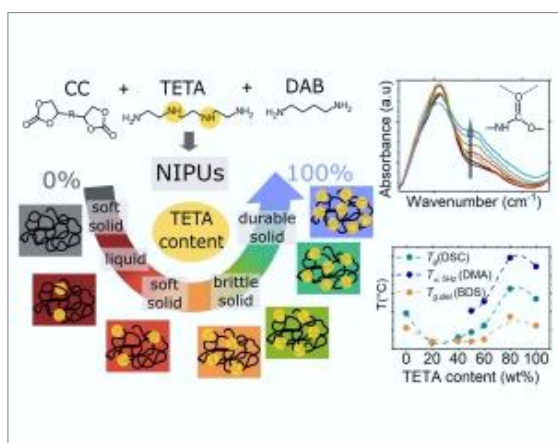
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- [2] Parzuchowski, P. G., Rokicki, G., Mazurek, M. Non-isocyanate polyurethanes: Synthesis, properties, and applications. *Polymers for Advanced Technologies*. 2015, 26(7), 707-761. <https://doi.org/10.1002/pat.3522>
- [3] Łukaszewska, I., Bukowczan, A., Raftopoulos, K. N., Pielichowski, K. Tailoring the physical properties of non-isocyanate polyurethanes by introducing secondary amino groups along their main chain. *Journal of Molecular Liquids*. 2023, 391, 1-12. doi:10.1016/j.molliq.2023.123263
- [4] Łukaszewska, I., Bukowczan, A., Raftopoulos, K. N., & Pielichowski, K. Water-polymer interactions and mechanisms of water-driven glass transition decrease in non-isocyanate polyhydroxyurethanes with varying hydration sites. *Polymer*. 2024, 302. doi: 10.1016/j.polymer.2024.127060



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Pretransitional effects in nanocolloids – paraelectric nanoparticles in nematogenic liquid crystal with transverse permanent dipole moment

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Abstract: Adding nanoparticles (NPs) to liquid crystals (LCs) is an easy and effective way to improve their properties, because liquid crystals are very sensitive to external factors/ exogenic impact. The influence of nanoparticles on the properties of liquid crystals is so significant that a new category — LC + NP nanocolloids and nanocomposites — has been established. Because of this, scientists have increasingly shown interest in liquid crystal-based nanocolloids. Although numerous papers have been published on the mentioned topic, just a few consider the influence of pretransitional fluctuations. The broadband dielectric spectroscopy (BDS) studies were conducted in MBBA (N-(4 Methoxybenzylidene)-4-butaniline) and nanocolloids with paraelectric BaTiO₃ dispersions to assess the impact of pretransitional fluctuations on static and dynamic dielectric properties. The analysis included the isotropic, nematic, and solid phases. The pretransitional anomalies were observed in all investigated phases, including the solid phase. In the isotropic phase, critical-like pretransitional behaviour was revealed by applying the distortion-sensitive analysis introduced by Aleksandra Drozd-Rzoska. The evolution of the dielectric constant in the nematic phase shows a split into two regions, with the crossover coinciding with the standard melting temperature. The temperature evolution of apparent enthalpy also showed critical-like features. Nanoparticles had a significant impact on all investigated properties.

Keywords: liquid crystals, broadband dielectric spectroscopy, nanocolloids

References

- [1] Drozd-Rzoska, A., Łoś, J., Rzoska, S.J. The dominance of pretransitional effects in liquid crystal-based nanocolloids: nematogenic 4 methoxybenzylidene-4'-butylaniline with transverse permanent dipole moment and BaTiO₃ nanoparticles. *Nanomaterials*. 2024, 14, 655, 1-24. doi:10.3390/nano1408065.
- [2] Starzonek, S.; Rzoska, S.J.; Drozd-Rzoska, A.; Czupryński, K.; Kralj, S. Impact of ferroelectric and superparaelectric nanoparticles on phase transitions and dynamics in nematic liquid crystals. *Phys. Rev. E*. 2017, 96 (2-1). doi: 10.1103/PhysRevE.96.022705.
- [3] Drozd-Rzoska, A., Starzonek, S., Rzoska, S.J., Kralj, S. Nanoparticle-controlled glassy dynamics in nematogen-based nanocolloids. *Phys. Rev. E*. 2019, 99 (5-1), doi: 10.1103/PhysRevE.99.052703

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Qualitatively and quantitatively different configurations of nematic– nanoparticle mixtures

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Abstract: We consider the influence of different nanoparticles or micrometre-scale colloidal objects, which we commonly refer to as particles, on liquid crystalline (LC) orientational order in essentially spatially homogeneous particle–LC mixtures.

We first illustrate the effects of coupling a single particle with the surrounding nematic molecular field. A particle could either act as a “dilution”, i.e., weakly distorting the local effective orientational field, or as a source of strong distortions. In the strong anchoring limit, particles could effectively act as topological point defects, whose topological charge q depends on particle topology. The most common particles exhibit spherical topology and consequently act as $q = 1$ monopoles. Depending on the particle’s geometry, these effective monopoles could locally induce either point-like or line-like defects in the surrounding LC host so that the total topological charge of the system equals zero.

The resulting system’s configuration is topologically equivalent to a crystal-like array of monopole defects with alternating topological charges. Such configurations could be trapped in metastable or stable configurations, where the history of the sample determines a configuration selection.

Keywords: nanoparticles; liquid crystals; topological charge

References

- [1] Schoffelen, S., van Hest J. C. M. Multi-enzyme systems: bringing enzymes together in vitro. *Soft Matter*. 2012, 8, 1736–1746. doi: 10.1039/c1sm06452e
- [2] Yuan, Y.; Smalyukh, I.I. Chiral, topological, and knotted colloids in liquid crystals. *Crystals*. 2024, 14, 885. <https://doi.org/10.3390/cryst14100885>
- [3] Harkai, S.; Murray, B.-S.; Rosenblatt, C.; Kralj, S. Electric field driven reconfigurable multistable topological defect patterns. *Phys. Rev. Res.* 2020, 2, 013176. doi: <https://doi.org/10.1103/PhysRevResearch.2.013176>

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Liquid crystalline phases of short guanine-rich DNA molecules

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Abstract: The DNA molecule represents a fundamental biological system whose basic shape is a double helix, which enables the storage of genetic information and the transfer of genetic material. However, in addition to the classical double helix structure, DNA can form higher-order structures such as DNA-quadruplexes. These are formed by the self-assembly of guanine-rich DNA sequences, where four guanine bases hydrogen bond together to form a G-quartet, which is the basic unit of a DNA-quadruplex. Quadruplexes can also form in chromosomes, where they play an essential role in gene regulation. Moreover, they are associated with various diseases, including neurodegenerative diseases such as amyotrophic lateral sclerosis and frontotemporal dementia. DNA quadruplexes can stack on top of each other and form long rodlike aggregates that can, at higher concentrations, exhibit a lyotropic liquid crystalline (LC) behaviour. In our study, we investigated the guanine-rich DNA sequences $d(G_4C_2)_n$ with $n = 1, 2, 4$, found in the non-coding region of the *C9orf72* gene. In previous studies, where we used dynamic light scattering (DLS) and atomic force microscopy (AFM), we confirmed that all three sequences form DNA quadruplexes. We determined the translational diffusion coefficients and the lengths of the aggregates formed in the solution. We found out that the sequence $d(G_4C_2)$ formed extremely long aggregates with lengths above 80nm. The sequence $d(G_4C_2)_2$ formed short stacked dimeric quadruplexes, approximately 3nm in length. The sequence $d(G_4C_2)_4$ formed aggregates with a length of about 10 nm, which corresponds to seven stacked monomolecular quadruplexes. In this research, we prepared concentrated aqueous solutions ($c > 10$ mM) of $d(G_4C_2)_n$ with $n = 1, 2, 4$, incorporated them into thin glass cells, and imaged them by using polarization optical microscopy (POM). We found that all three sequences showed extensive orientational ordering of DNA-quadruplex aggregates and the formation of LC phases. Different LC textures resulted from different lengths of the DNA-quadruplex assemblies, which is characteristic of chromonic LCs.

Keywords: DNA molecule, orientational ordering, liquid crystalline

References

- [1] Livolant, F.; Levelut, A.-M.; Doucet, J.; Benoit, J.-P. The highly concentrated liquid-crystalline phase of DNA is columnar hexagonal. *Nature*. 1989, 339(6227), 724–726. doi: 10.1038/339724a0.
- [2] Potrč, M.; Sebastián, N.; Škarabot, M.; Drevenšek-Olenik, I.; Spindler, L. Supramolecular polymorphism of $(G_4C_2)_n$ repeats associated with ALS and FTD. *International Journal of Molecular Sciences*. 2021, 22(9) 4532. doi: 10.3390/ijms22094532

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Spatial manipulation of topological defects in nematic shells

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Abstract: It is well established that the positions of topological defects (TDs) in liquid crystals can be experimentally manipulated by locally distorting the liquid crystalline (LC) order — for example, through localized melting induced by optical tweezers. The simplest nematic LCs consist of anisotropic (e.g., rod-like) molecules and exhibit liquid-like behavior combined with orientational order. The latter is typically described at the mesoscopic level by the nematic director field \mathbf{n} , which points along the local average molecular orientation. In bulk equilibrium, \mathbf{n} is spatially homogeneous and aligned along a single symmetry-breaking direction. Nematic shells represent effectively two-dimensional (2D) systems in which the orientations of \mathbf{n} are confined within a curved 2D surface. As a consequence, such structures are generally dominated by topological defects. In this work, we numerically investigate the nematic ordering profiles and the corresponding topological defect (TD) configurations in thin nematic LC shells subjected to locally imposed distortions of the LC order. We demonstrate that, within curved LC films, such manipulations can be strongly influenced by the local Gaussian curvature, particularly when it exhibits pronounced spatial variations. A mesoscopic theoretical framework is employed, in which both the shell geometry and the LC orientational order are described through the surface curvature and the nematic order parameter tensor. For illustration, we consider LC shells of spherical topology. Our results show that, with increasing shell prolateness—which introduces spatially inhomogeneous Gaussian curvature—the topological defects become increasingly “anchored” to regions of characteristic local curvature.

Keywords: topological defects, liquid crystalline

References

- [1] Smalyukh, I. I. Knots and other new topological effects in liquid crystals and colloids. *Reports on Progress in Physics*. 2020, 83(10), doi:<https://doi.org/10.1088/1361-6633/abaa39>
- [2] Kralj, S., Rosso, R., & Virga, E. G. Curvature control of valence on nematic shells. *Soft matter*. 2011, 7(2), 670–683. <https://doi.org/10.1039/C0SM00378F>
- [3] Kralj, S., Murray, B. S., & Rosenblatt, C. Decomposition of strongly charged topological defects. *Physical Review E*. 2017, 95(4), 042702. doi: 10.1103/PhysRevE.95.042702

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Phase equilibria and critical behavior in nematogenic MBBA–isooctane monotectic type mixtures.

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Abstract: Lecture based on the study by Kalabiński, Drozd-Rzoska, and Rzoska, which investigates in detail the monotectic-type phase behavior of nematogenic MBBA–isooctane mixtures, combining phase-diagram construction, coexistence-curve analysis, and nonlinear dielectric effect (NDE) measurements. The complete phase diagram reveals two distinct biphasic regions: TP1, corresponding to isotropic–nematic coexistence at low isooctane content, and TP2, associated with liquid–liquid separation at high isooctane concentrations. These two domains provide a unique opportunity to analyze orientational and compositional criticality within the same binary system. A central achievement of the study is the quantitative parameterization of the coexistence curves. For TP1, the authors demonstrate that the isotropic–nematic coexistence width follows the scaling relation, with two composition-dependent regimes. For TP2, the analysis of the binodal reveals an anomalous evolution of the effective order-parameter exponent β_{eff} , which increases when approaching the consolute temperature. This behavior differs from classical binary mixtures and is attributed to the uniaxial molecular anisotropy of MBBA, which enhances mean-field-type features near the critical point. Such behavior is consistent with previous observations of anisotropic fluctuation dynamics by S.J. Rzoska and collaborators.

The study also provides rare photographic documentation (Figures below) of two distinct types of precritical opalescence. Near TP1, a transient milky turbidity appears despite the absence of a classical critical point, whereas TP2 exhibits a wide temperature range of critical opalescence extending 10 K above the consolute temperature. This effect indicates that orientational and density-driven fluctuations strongly couple in LC–solvent systems.

Further support comes from NDE measurements, performed with exceptional sensitivity, reaching values as low as $10^{-19} \text{ m}^2\text{V}^{-2}$. For TP1, the NDE pretransitional effect follows mean-field behavior with exponent $\psi = 1$, while near TP2 it shows mixed-criticality signatures typical of classical liquid–liquid demixing. These observations validate the theoretical interpretation and align with earlier NDE investigations by Rzoska and co-workers.

Overall, the scientific value of this investigation is high: it provides one of the most detailed quantitative analyses of monotectic-type LC mixtures to date, identifies previously unreported anomalies in binodal behavior, validates fluctuation-driven phenomena using ultrahigh-sensitivity NDE, and establishes MBBA–isooctane mixtures as a model system for studying universal features of limited miscibility in anisotropic fluids.

Keywords: monotectic, mean-field behavior, binodal

References

- [1] Kalabiński, J.; Drozd-Rzoska, A.; Rzoska, S.J. Phase equilibria and critical behavior in nematogenic MBBA–Isooctane monotectic-type mixtures. *Int. J. Mol. Sci.* 2023, 24, 2065. <https://doi.org/10.3390/ijms24032065>
- [2] Rzoska, S.J.; Chrapeć, J.; Ziolo, J. Nonlinear dielectric effect in a pure and in a nitrobenzene-doped critical solution of perfluoromethylcyclohexane–carbon tetrachloride. *J. Phys. Chem.* 1988, 92, 2064–2066. <https://doi.org/10.1021/j100318a071>

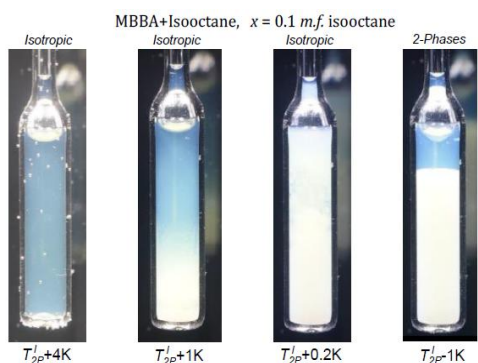
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- [3] Drozd-Rzoska, A.; Rzoska, S.J.; Rzoska, A.A. Pretransitional Behavior of Nonlinear Dielectric Effect for the Liquid–Solid Transition in Nitrobenzene. *Phys. Rev. E*. 2016, 93, 06213. <https://doi.org/10.1103/PhysRevE.93.06213>
- [4] Rzoska, S.J.; Drozd-Rzoska, A. Dual-Field Nonlinear Dielectric Spectroscopy in a Glass-Forming EPON 828 Epoxy Resin. *J. Phys.: Condens. Matter*. 2011, 24, 035101. <https://doi.org/10.1088/0953-8984/23/3/035101>



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Slave-master mechanism of nematic liquid crystals

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Abstract: We introduce the slave-master mechanism in the phase behavior of two-component systems where both components could exhibit some kind of (quasi) long-range order. The key feature of the mechanism is that one component strongly influences the other, while the reverse influence is negligible. To illustrate the effect, we consider systems where each isolated component exhibits an order-disorder phase transition on varying a control parameter (e.g., temperature) to which we refer as the generalized temperature. We present a minimal model that shows robust slave-master behavior. As exemplary systems, we present thermotropic liquid crystals (LCs) exhibiting nematic and smectic A phase order, focusing on the interaction strength between orientational and translational order. Mixtures of nematic LC molecules and anisotropic nanoparticles are also presented. We show that qualitatively different behaviors could emerge via the specific nature of the inter-component interaction. Mastering this mechanism could lead to various applications based on phase tunable properties.

Keywords: phase behavior, liquid crystals, nanoparticles, mesoscopic modeling, slave-master behavior

References

- [1] Hölbl, A., Kaushik Pal, K., Slavinec, M., Kralj, S. Slave-master mechanism of thermotropic liquid crystal phase transitional behavior, *Physica B: Condensed Matter*. 2022, 642, 414142. doi: <https://doi.org/10.1016/j.physb.2022.414142>
- [2] Hegmann, T., Qi, H., Vanessa M. Marx, V., M. Nanoparticles in liquid crystals: synthesis, self-assembly, defect formation and potential applications, *Journal of Inorganic and Organometallic Polymers and Materials*. 2007, 17(3) 483-508. doi:10.1007/s10904-007-9140-5

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Complexity of nematic liquid crystal configurations

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Abstract: Of our interest are frustration-driven pattern generating mechanisms in systems which in bulk equilibrium display spatially homogeneous long-range orientational order in absence of perturbations. As testbed material, we select thermotropic nematic liquid crystals. In bulk, they exhibit weakly discontinuous order-disorder phase transformation on varying temperature where the ordered nematic phase features spatially uniform axial order along an arbitrary symmetry breaking direction. However, due to continuous symmetry breaking (CSB) the established order is extremely susceptible to various perturbations which are in real systems in general always present. We theoretically illustrate how diverse complex patterns could be excited. Particularly intriguing configurations could appear if topological defects are present that could be generated via CSB. Our analysis is based on a relatively simple Lebwohl-Lasher-type model in which we could get analytical insight into phenomena of our interest. Using it we illustrate history dependent early stage I-N evolution and final patterns in presence of “impurities” (e.g., nanoparticles). We show how characteristic effective interaction characteristics predict qualitatively different emerging patterns. Our analysis is based on CSB which is ubiquitous in nature. Consequently, demonstrated mechanisms are expected to manifest also in other condensed matter systems whose ordered phase is formed via CSB.

Keywords: continuous symmetry breaking, patterns, topological defects, nematic liquid crystals

References

- [1] Kralj, S., Majumdar, A., Order reconstruction patterns in nematic liquid crystal wells. *Proc. R. Soc. Lond. Ser. A – Math. Phys. Eng. Sci.* 2014, 470(2169), 1-18. <https://doi.org/10.1098/rspa.2014.0276>
- [2] Selinger, J. V. Director deformations, geometric frustration, and modulated phases in liquid crystals. *Annual Review of Condensed Matter Physics.* 2022, 13, 49-71. <https://doi.org/10.1146/annurev-conmatphys-031620-105712>

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Theoretical and experimental study of elastocaloric responses in liquid crystalline elastomers

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Abstract: We carry out a systematic experimental and theoretical study of elastocaloric (eC) response in nematic liquid crystal elastomers (LCEs), which possess the elastic properties of elastomers combined with the orientational order of liquid crystals. The chemical linking of mesogens to the polymer backbone enables a thermomechanical response yielding a large spontaneous change in the LCE geometry on varying the temperature. In liquid crystal elastomers a relatively large eC effect could be obtained upon adiabatic application or removal of a stress field in the isotropic state near phase transformation to the more ordered state. In these cases, the change in isothermal entropy or adiabatic temperature is compensated by a temperature change in liquid crystal elastomers. This effect can be exploited towards soft condensed state cooling technologies that are gaining increasing interest due to environmental issues, low cost, and low stimulus field. We present directly measured elastocaloric temperature changes. Experimental measurements are interpreted using a modified Landau-de Gennes mesoscopic model taking into account both internal and external stress fields. Our systematic study identifies conditions yielding responsivity of a few K/MPa, which is two orders of magnitude larger than in the shape memory alloys, the most intensively studied materials for this effect.

Keywords: mesogens, liquid crystal elastomers, elastocaloric response

References

- [1] Moya X., Mathur., N.D. Caloric materials for cooling and heating *Science*, 2020, 370 (80), 797-803. doi: 10.1126/science.abb0973.
- [2] Liu, J., Zhao, D., Li Y. Exploring magnetic elastocaloric materials for solid-state cooling. *Shape Mem. Superelasticity*. 2017, 3, 192-198, doi: 10.1007/s40830-017-0118-z

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Impact of the linking bridge type on self-assembly behavior of difluorosubstituted terphenyls

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Abstract: The self-assembly behaviour and crystallization kinetics of two liquid-crystalline materials containing a 2',3'-difluorosubstituted terphenyl mesogenic core have been examined in detail. Calorimetric analyses reveal that the nature of the linking bridge plays a crucial role in determining the polymorphism of the smectic phases. The CH₂O.3 compound, incorporating a –CH₂O– bridge and a longer methylene spacer, displays a chiral smectic SmC_A* phase with antiferroelectric properties. In contrast, the COO.6 compound, which contains a –COO– bridge and a shorter alkyl chain, develops a chiral smectic SmC* phase exhibiting ferroelectric properties. Both materials crystallize during slow cooling, whereas rapid cooling favours vitrification of a conformationally disordered crystal phase. Dielectric spectroscopy reveals intricate relaxation dynamics across the observed thermodynamic states, while DFT calculations provide insight into the molecular origin of these processes. The results obtained may prove important for advancing research on liquid-crystalline systems and their prospective applications. Nonetheless, further studies are required to clarify how mesophase organization relates to crystallization, vitrification, and the associated kinetic phenomena.

Keywords: mesogens, liquid crystal elastomers, elastocaloric response

References

- [1] Moya X., Mathur., N.D. Caloric materials for cooling and heating *Science*. 2020, 370 (80), 797-803. doi: 10.1126/science.abb0973.
- [2] Liu, J., Zhao, D., Li Y. Exploring magnetic elastocaloric materials for solid-state cooling. *Shape Memory and Superelasticity*. 2017, 3, 192-198, doi: 10.1007/s40830-017-0118-z
- [3] Drzewicz, A., Jasiurkowska-Delaporte, M., Kula, P., E. Juszyńska-Gałązka, Effect of the linking bridge type on the self-assembly behaviour of 2',3'-difluoroterphenyl derivatives, *Physical Chemistry Chemical Physics*. 2024, 26, 8748-8760. <https://doi.org/10.1039/D4CP00133H>
- [4] Herman, J., Aptacy, A., Dmochowska, E., Perkowski, P., Kula, P. The effect of partially fluorinated chain length on the mesomorphic properties of chiral 2',3'-difluoroterphenylates. *Liquid Crystals*. 2020, 47(1), 1-9. doi: 10.1080/02678292.2020.1811410

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CLOSING LECTURE

The 3rd International Seminar on Soft Matter: Conclusions & Remarks

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Abstract: In 1991 Pierre Gilles de Gennes presented the Nobel Prize lecture entitled 'Soft Matter' which created a new category of systems, linking liquid crystals, polymers, colloids, supercooled liquids, micellar mixtures, Their common feature is the dominance of mesoscale species, in time & space, in comparison with standard materials governed mainly by properties below nanometrics and nanoseconds scale. It leads to enormous sensitivity to exogenic factors (pressure, electric field, etc.) and endogenic factors, such as nanoparticles and solute admixtures. This seminar addresses these issues, with a significant focus on topological aspects, which are ideal for direct experimental observation precisely because this phenomenon occurs at a mesoscale. The seminar largely focused on biologically significant systems and liquid crystals affected by nanoparticles. Another significant area of research was the transition to the glass state, with a particular focus on the effects of high pressure. The seminar also provided young researchers with the opportunity to learn about one another's scientific works and to present their own achievements. A special session entitled "*Show Yourself in Science*" demonstrated the purposefulness and practical tools for promoting one's results. This will further enable conscious and purposeful planning of research and personal development paths.

It would be a great pleasure to see you again at our upcoming online edition of
4th Polish-Slovenian International Seminar on Soft Matter

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