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***Chronicle***

# Planer-Smoluchowski Soft Matter Workshop on Liquid Crystals and Colloidal Dispersions

Liquid crystals and colloidal dispersions are of vital importance for technological applications and practical devices. Nowadays the high-quality displays, non-mechanical beam steering devices, and switching elements in optical telecommunication networks can hardly be imagined without liquid crystals. Liquid crystals composed of (or doped by) nano-sized particles are of interest for a possible utilization in the emerging novel applications such as tunable and frequency selective negative index media. The anticipated new technological developments are closely related to a number of interesting problems in basic science of liquid crystal colloids that attract a great deal of current interest.

The Planer-Smoluchowski Soft Matter (PSSM) Workshop on Liquid Crystals and Colloidal Dispersions was held on June 22, 2009 in historic city of Lviv in Ukraine. The names of Planer and Smoluchowski in the title of workshop as well as the city of Lviv as host are not accidental. Two outstanding scientists – Julius Planer and Marian Smoluchowski – both have made pioneering contributions to the modern understanding of liquid crystals and colloidal dispersions when they used to live and work [during different periods of time] in city of Lviv. **Julius Planer** was born in 1827 in Vienna and moved to Lviv in 1855 where till 1863 he headed Department of Anatomy at Lviv University. Among others, in 1861 Planer published a paper in which he reported the first experimental observations of the mesomorphic phase behavior and what is now known as thermotropic liquid crystal. **Marian Smoluchowski** was born in 1872 near Vienna and in 1899 came to Lviv where he stayed till 1913 occupying different positions at Lviv University. Here in Lviv Smoluchowski made many contributions to the physics of condensed matter. Particularly, in 1904 he was the first who noted the existence of density fluctuations in the gas phase. In 1906, independently of Albert Einstein, Smoluchowski found the theoretical explanation of Brownian motion, the piece of work for which today he is best known. In 1908 Smoluchowski became the first physicist to ascribe the phenomenon of critical opalescence to large density fluctuations. Thus, besides the scientific goals PSSM Workshop on Liquid Crystals and Colloidal Dispersions celebrated the legacy of these two outstanding scientists Julius Planer and Marian Smoluchowski, who both made pioneering contributions to the understanding of these classical soft condensed matter systems.

The PSSM workshop was organized by the Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine and the University of Colorado at Boulder and brought together prominent scientists working at the forefronts of soft materials science and statistical physics, postdoctoral fellows and students from around the world. The workshop was supported by Ivan Franko National University of Lviv (modern name of the same Lviv University where both fellow men used to work) and International Institute for Complex Adaptive Matter (ICAM-I2CAM). ICAM-I2CAM is a distributed experiment-based multi-institutional partnership whose purpose is to identify major new research themes in complex adaptive matter – the search for an understanding of emergent behavior in hard, soft, and living matter. The PSSM workshop in Lviv was the first workshop sponsored by ICAM-I2CAM in the Eastern Europe.

The one-day program of the workshop was quite intense, being composed of 6 invited lectures, 10 oral presentations as well as 16 poster presentations discussed during the lunch break. All workshop events took place in the main building of the Ivan Franko National University of Lviv and, particularly, in a beautiful Conference Hall formerly used by the Galician parliament. Invited lectures were delivered by Slobodan Žumer from the University of Ljubljana, Matt Glaser from the University of Colorado at Boulder, Matthias Ballauff from the University of Bayreuth in Germany, Pawel Bryk from Maria Curie-Sklodowska University in Lublin, Liang-Chy Chien from Kent State University and Pawel Pieranski from the University of Paris-Sud.

Slobodan Žumer presented a lecture on the formation of complex assemblies of particles in nematic phases. Description based on a Landau type approach coupled with topological theory provides a useful tool for modeling these complex structures. Spacial emphasis was laid upon recent modeling achievements that are contrasted with the latest experimental studies. In solvents, where nematic order is present, an effective long-range interparticle coupling appears. It leads to numerous organizations of colloidal particles not present in simple liquids. Of particular interest are situations where topological constraint causes the sharing of a disclination by neighboring particles which leads to a string-like coupling. Colloidal dimmers, chains, lattices, braids, and hierarchal structures can be realized via disclination loops with singular or non-singular cores. Authors expect that some of these structures will open new ways to the assembling of complex structures needed for metamaterials.

Matt Glaser spoke on simulation studies of spherical nanoparticles in a nematogenic solvent consisting of soft spherocylinders. Authors found that nanoparticles remain well dispersed in the isotropic (low-density) phase of the solvent, but demix into a nanoparticle-poor nematic phase and a nanoparticle-rich isotropic phase at higher pressures. When the nanoparticle-spherocylinder interactions are modified to promote homeotropic anchoring, the solvent-induced interaction between nanoparticles in the isotropic phase exhibits strong intermediate-range repulsion that is expected to further stabilize nanoparticle dispersions. However, many-body effects appear to dominate nanoparticle-nanoparticle interactions in the isotropic phase with homeotropic anchoring even at the lowest nanoparticle concentration investigated, resulting in suppression of the intermediate range repulsion and leading to nanoparticle aggregation. The effective interactions between nanoparticles in nematogenic media are similar to depletion interactions in colloidal systems, suggesting a strong analogy between nanoparticles in thermotropic liquid crystals and lyotropic mixtures of colloidal spheres and rods.

In his lecture Matthias Ballauff proposed a new way to determine weak repulsive forces operating between colloidal particles by measuring the rate of slow coagulation. According to Smoluchowski's classical paper, the rate of slow coagulation is directly related to the competition of the repulsion with thermal motion. Since the thermal forces are weak, measurements of the coagulation rate can provide precise information on repulsive potentials having a magnitude of just a few $kT$. This novel way was illustrated by studying colloidal spherical polyelectrolyte brush particles in aqueous solution containing trivalent $La^{3+}$ counterions. The particles consist of a monodisperse polystyrene core of 121 nm radius from which linear sodium poly(styrene sulfonate) chains are densely grafted (contour length: 48 nm). Authors determined the rate of coagulation by time-resolved simultaneous static and dynamic light scattering in presence of $LaCl_3$. Direct measurements of the repulsive forces between macroscopic brush layers demonstrate that the potential decays exponentially with distance. This is in good agreement with a simple theoretical treatment that furthermore leads to the effective surface potential and underscores the general validity of the approach.

Pawel Bryk from Maria Curie-Sklodowska University in Lublin, Poland, spoke on theoretical investigations of effective interactions in colloidal suspensions. The bare interactions between macroparticles are attractive at larger separations due to the dispersion forces between the atoms forming the colloidal particles. In order to prevent aggregation, the colloidal suspension should be stabilized either by charge or sterically. Technological developments during the last two decades made it possible to prepare well-defined colloidal suspensions. With the help of video-microscopy and total internal reflection microscopy effective interactions in colloidal suspensions can be measured directly, and compared with theoretical predictions. Author presented the results of investigations of the effective interactions in colloidal systems using modern liquid-state theories. He also discussed the depletion interactions between a large colloidal particle, immersed in a "sea" of smaller colloidal particles, and various substrates. The large colloidal particle was modeled as a hard sphere, and the substrate has a certain geometrical (like a wedge, or an edge, or a regular pattern created by decorating a structureless wall by hemispheres), or thermodynamical feature (like semipermeability to some of the components of a multicomponent mixture). These results were discussed in the context of possible experimental realizations of such systems. The issue of the onset of polydispersity on the effective interactions in colloidal suspensions with the attractive/repulsive bare interactions was addressed as well.

Liang-Chy Chien spoke on tunable cholesteric liquid crystal color. It is known that cholesteric liquid crystals (CLCs) in the planar texture possess a unique feature of separating incident light into its left- and right-handed circular components by reflecting one component and transmitting the other. In a planar aligned CLC with a preselected helical pitch only a single wavelength can be Bragg reflected (monochrome). In addition to the temperature dependence of Bragg reflected wavelength of a CLC, there are two ways to prepare multiple wavelength (or color) reflecting CLCs; one method is by stacking multiple layers of CLCs with different cholesteric pitches to reflect different wavelengths. In this case, the stacking is normally arranged in a fashion that CLC reflecting a shorter wavelength is placed on top and the CLC reflecting a longest wavelength is placed at the bottom of the stacked films. Alternatively, multiple (wavelengths) colors reflection CLCs can be obtained in sequential arrangement in a single layer with CLCs, reflecting different wavelengths or colors. A couple of approaches in tuning the cholesteric color were reported.

Pawel Pieranski presented a lecture on universal aspects of liquid crystals. Among others he focused on a few selected topics that can be of interest also for non-specialists. In particular, he spoke about Mark Kac (a famous mathematician from the Lviv School of Mathematics) and the issue of isospectral drum initiated by him.

The short oral presentations focussed on recent advances bridging a gap between basic soft condensed matter physics and applied science. In particular, Longin Lisetski from the Institute for Scintillation Materials, STC “Institute for Single Crystals” of the National Academy of Sciences of Ukraine delivered a collection of results obtained by using a model approach to molecular-statistical description of liquid crystal phases with helical twisting and supramolecular heterostructuring. Among the most convincing examples (which have not been paralleled by other known theoretical descriptions of liquid crystal properties), one can note the following: (i) straightforward explanation of substantially different helical twisting values and even different helical twisting sense of, e. g. cholesteryl chloride and cholesteryl alkanoates (which have very close values of optical rotation); (ii) numerous cases of extra helical twisting induced in cholesteric matrices by introduction of non-chiral and non-mesogenic dopants, even in the absence of apparent specific interactions; (iii) anomalous increase in the nematic phase thermal stability for certain mixtures containing components of different chemical nature, etc. It was claimed that the proposed approach can be very promising for a description of recently discovered and developed liquid crystalline systems characterized as nanostructured or heterostructured ones (including liquid crystalline dispersions of carbon nanotubes, nanorods and other shaped particles of organic and inorganic functional materials, etc.).

Qingkun Liu from the Zhejiang University in China was talking about the assembly and alignment of plasmonic nanoparticles by lyotropic liquid crystals, which follows from the studies of self-assembly and self-alignment of the gold nanorods dispersed in nematic and hexagonal lyotropic liquid crystals. He also has discussed the novel plasmonic effects arising from the unidirectional ordering of gold nanorods in these soft materials.

Yves Lansac from the Universite Francois Rabelais, Tours, France showed the results of coarse-grained and atomistic simulations of calamitic and bent-core liquid crystals aimed at characterizing nanophase segregation in smectics and exploring the molecular origins of tilt, spontaneous chirality, polarization splay, and saddle-splay layer curvature in bent-core liquid crystals. It was found that minimal models, incorporating the excluded volume interactions and differential intramolecular flexibility, display most of the commonly observed smectic phases, including smectic C and tilted hexatic phases of calamitic molecules, and spontaneously chiral and polarization splay modulated (B1 and B7) phases of bent-core molecules. These findings suggest that thermotropic smectics can be understood as flexibility or shape amphiphiles, in strong analogy to lyotropic liquid crystals.

Jaroslav Ilnytskyi from the Institute for Condensed Matter Physics, Lviv, Ukraine, discussed what can be achieved by molecular dynamics simulation of liquid crystalline polymers. To illustrate this he presented three groups of results obtained quite recently. The first one concerns molecular dynamics simulations of liquid crystalline dendrimers in isotropic, nematic and smectic A solvent. Authors concentrate on orientational relaxation of the macromolecule and its equilibrium shape depending on the phase of the solvent and the way the terminal mesogens are attached to the dendritic core. The presented results are relevant in terms of the relation between the molecular shape and bulk phase. The second problem addresses the origin of photo-induced deformations in azobenzene-containing polymer films. Authors reproduced the opposite sign of the deformations under uniform linearly polarized light in liquid crystalline and amorphous films, respectively. The simulations shed some more light on underlying microscopic mechanisms of these deformations. The third problem is the memory effects in liquid crystalline elastomers that are potentially attractive for being applied as artificial muscles. Using molecular dynamics simulations the authors reproduced the reversibility of the shape of lightly crosslinked melt of polymer liquid crystal when driven via the smectic-isotropic transition. The presented examples demonstrate the possibilities of molecular dynamics simulations in clarifying the microscopic mechanism behind various effects and are a starting point for simulation driven predictions of the properties of new materials.

Shape controlled colloidal interactions in anisotropic fluids were reported by Clayton Lapointe from University of Colorado at Boulder. Colloidal particles suspended in nematic liquid crystals are known to exhibit highly directional interactions mediated by the elasticity of the liquid crystal. Using lithographically fabricated platelet colloids, having equilateral polygonal shapes, the authors showed that colloids with an even number of sides form elastic quadrupoles whereas those with an odd number of sides form elastic dipoles. These qualitatively different interactions lead to self-assembled structures that reflect the shape-dependent symmetries of elastic deformations in the liquid crystal, demonstrating that colloidal interactions can be effectively controlled through particle shape. The observed dipolar configuration requires no bulk topological defects, indicating that dipole-dipole elastic interactions can be scaled down to submicron sizes, which is not possible with spherical inclusions.

Colloidal nematostatics was presented and discussed by Victor Pergamenshchik from the Institute of Physics of the National Academy of Sciences of Ukraine in Kyiv. Colloids interact via the nematic director. As the interaction is of a long range, the nematic colloids are much closer to electrostatic systems than to standard colloids in isotropic liquids. The author was talking about an elastic "charge" and elastic multipoles, about their interaction and odd properties, e. g., elastic charge is a vector, elastic dipole can be chiral, etc.

The report by Akihiko Matsuyama from Kyushu Institute of Technology in Japan was devoted to the problem of phase separations in mixtures of a liquid crystal and a colloidal particles by means of a mean-field theory. By taking into account a nematic and a smectic A ordering of liquid crystals and a crystalline ordering of colloidal particles, the authors calculated the phase diagrams on the temperature-concentration plane. They predict various phase separations, such as a smectic A-crystal phase separation and a smectic A-nematic-crystal triple point, etc., depending on the interactions between a liquid crystal and a colloidal surface. Inside binodal curves, authors found new unstable and metastable regions which are important in the phase ordering dynamics. The authors also found a crystalline ordering of colloidal particles dispersed in a smectic A phase and in a nematic phase. The cooperative phenomena between liquid crystalline ordering and crystalline ordering induce a variety of phase separations.

Stanislav Chernyshuk from the Institute of Physics of the National Academy of Sciences of Ukraine in Kyiv, reported the results on a direct observation of the photochemical switching between colloidal crystals with different lattice constants in a liquid-crystal emulsion. Glycerol droplets being introduced in a nematic liquid crystal form two-dimensional hexagonal colloidal crystal at the nematic-air interface with a lattice constant depending on the surface tension. The authors dope an azobenzene derivative into the liquid crystal emulsion to modulate the colloidal structures by using cis-trans photoisomerization of the doped dye. The photoisomerization changes the surface tension and the lattice constant of colloidal crystals with a relaxation time $T$ about 10 $s$. A simple theoretical description was proposed, which qualitatively agrees with experimental results. Possible applications of photonic crystals in infrared range were discussed. The number $N$

of different kinds of dyes set the number of different possible photonic crystals as $2^N$, which may be transformed one into another by corresponding $2N$ light beams, inducing cis-trans photoisomerization of the doped dyes.

Jozef Spalek from Jagiellonian University in Krakow, Poland, presented a brief story on Marian Smoluchowski in life and science. Finally, the report by ICAM-I2CAM Co-Director Daniel Cox from the University of California at Davis was concerned the opportunities offered by ICAM-I2CAN to nucleate and expand collaborations with US institutions.

It is important to note, that all presentations of the PSSM workshop were webcast in real time and, in addition to the audience in the Conference Hall in Lviv, registered participants around the world were able to participate, asking questions immediately after presentations. We conclude, that being at the nexus of material science and soft condensed matter physics, the workshop theme turned out to be inherently interdisciplinary and the PSSM Workshop enabled the researchers working at the forefronts of basic and applied material science to discuss the recent advances in the field of liquid crystals and colloidal dispersions.

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