## Foreword

## Liquid crystal colloids

This special issue of "Condensed Matter Physics" focuses on the most recent developments in the study of a fascinating soft matter system, representing colloidal particles in a liquid crystalline environment. The bulk and surface properties of a liquid crystal as a dispersive medium are determined by anisotropic molecular interactions. In the bulk, these interactions establish the liquid crystalline phases with a long-range orientational order and no (or partial) positional order. In an equilibrium "monocrystalline" state, the director  $\mathbf{n}$  describing the average molecular orientation in space is uniform. At the interface between the colloidal particle and the liquid crystalline host, the anisotropy of molecular interactions causes director distortions. For example, a sphere with a perpendicular orientation of liquid crystal molecules at its surface will tend to create a hedgehog-like configuration around itself. Whether or not such a radial configuration will be stabilized, depends on the material parameters, namely, the typical elastic constant K associated with the director gradients and the surface anchoring coefficient W describing how much work one needs to do in order to realign the director over the surface of a unit area by, say, 90 degrees. The ratio  $\xi = K/W$ is of the dimension of length. The constant K can be estimated as  $K \sim k_{\rm B}T/a \sim 10$  pN, where  $a \sim 1$  nm is the typical molecular length and T is the room temperature close to which most liquid crystals melt. Rather surprisingly, W is typically much smaller than a naive expectation  $k_{\rm B}T/a^2$ ; its experimental values range from  $10^{-6}$  J/m<sup>2</sup> to  $10^{-3}$  J/m<sup>2</sup>, resulting in the values of  $\xi$ from 10 nm to 10  $\mu$ m. In other words, a typical  $\xi$  is much larger than the molecular dimension and is within the range associated with the size of particles in colloidal systems. This feature makes it possible to distinguish two types of liquid crystal colloids (LCCs).

When the typical size of particles R is much smaller than  $\xi$ , one deals with the LCC in which the director is not strongly pinned at the inclusions; if the initial liquid crystal orientation is monocrystalline, it is likely to remain as such even if the small particles  $R \ll \xi$  are added. Although the director orientation does not change much, the small particles still impart new properties on the composition, through their contributions to the effective elastic, viscous, dielectric and optical anisotropy, etc. The additives-modified molecular interactions can also change the overall director structure. A good example is an addition of chiral molecules  $(R \sim a)$  to a nematic liquid crystal that transform it into the so-called cholesteric liquid crystal with a helicoidal director configuration. We can refer to the system with  $R \ll \xi$  as LCC with weak intrinsic anchoring.

When the inclusions are much larger than  $\xi$ , the situation changes dramatically. In the first approximation, the energy of elastic distortions  $\sim KR$  scales linearly with R, while the surface contributions are quadratic in R. As a result, each particle tends to satisfy the boundary conditions imposed by the anisotropic surface anchoring potential, at the expense of the elastic distortions in the surrounding liquid crystal. Generally, the elastic distortions culminate in the appearance of topological defect in the neighborhood of each and every particle that ensure the overall stability of the system and control its dynamics. The elasticity of distortions determines the interactions between the embedded particles, particles and the bounding walls, etc. The corresponding longrange forces have no analogues in regular colloids with an isotropic fluid as a dispersive medium. These systems can be referred to as LCCs with strong intrinsic anchoring. Their description is challenging, as it requires one to treat the complex 3D configurations of the director field, taking into account the boundary conditions at all the interfaces. A conceptual approach to the description of LCCs is to use an analogy with electrostatics, since in both cases one deals with long-range forces.

The issue presents the studies of both types of LCCs. Two articles focus on LCCs with strong intrinsic anchoring. Tasinkevych and Andrienko give a brief account of theoretical, computational, and experimental studies of LCCs, with a particular emphasis on the confined systems and the cases when the colloidal particles are only partially surrounded by the liquid crystalline host, e.g., being located at the free surface of a liquid crystal, or being embedded into a thin liquid crystalline film. The latter case is easy to carry out experimentally by drawing a freely suspended film of smectic liquid crystals. Interactions of particles in these films are especially rich since the orientation order within the films can be controlled by temperature and by phase transitions among various smectic phases. Pergamenshchik and Uzunova present a theory of "colloidal nematostatics" developed to describe large distance director-mediated interactions between the colloidal pairs and between a colloid and a bounding wall. The work classifies all possible types of elastic dipoles around inclusions of various shapes, derives potentials of Coulomb-like, dipole-dipole and quadrupole-quadrupole pair interactions, and presents formulae for particle-wall interactions that depend on the type of surface anchoring. Kurochkin et al. present an experimental study of a LCC with a weak intrinsic anchoring. They demonstrate that a liquid crystal doped with ferroelectric nanoparticles dramatically changes its basic thermodynamic features, such as the temperature of phase transitions.

Brodin et al. use the two-dimensional LCCs with strong intrinsic anchoring as a model system to explore the melting of a 2D periodic lattice. They deposit droplets of glycerol onto the surface of the liquid crystal. In a certain range of parameters, the droplets form a periodic array with hexagonal order, stabilized by the elasticity of the liquid crystalline background. By changing the temperature, one observes a spectacular effect of melting of this lattice that occurs at temperatures about 10 degrees lower than the temperature of liquid crystal-isotropic phase transition. Ilnytskyi et al. present a coarse-grained simulation model for a third generation liquid crystalline dendrimers. For the first time this allows for a successful molecular simulation study of a relation between the shape of a polyphilic macromolecular mesogen and the symmetry of the macroscopic phase. In the article by Holovko the traditional formalism in the liquid state theory based on the calculation of the pair distribution function is reviewed and generalized for nematic fluids. The heart of this approach is the solution of orientationally inhomogeneous Ornstein-Zernike equation in combination with the Triezenberg-Zwanzig-Lovett-Mou-Buff-Werheim equation. It is interesting and important that in the case of orientational inhomogeneity the system of these two equations allows an analytical solution to be carried out.

Finally, there are four short articles in this issue of "Condensed Matter Physics" that present a fascinating account of the pioneering steps in the discovery of liquid crystals. In 1861, Prof. Julius Planer, at that time a professor at Lviv University, published a note which for the first time detailed the quintessential liquid crystalline features. He synthesized cholesteryl chloride, a material that is broadly known nowadays to form a liquid crystalline phase of cholesteric type upon cooling from the isotropic phase. Almost one and half century ago, Planer observed an unusual optical property: in a certain temperature range, the molten material exhibited a violet color in reflected light and yellowgreen color in the transmitted light. The feature is typical of the cholesteric liquid crystal with helicoidal arrangement of molecule, having a submicron pitch that leads to the so-called "selective light reflection". To prove the point, Lisetckii (who has discovered the publication by Planer in late 1980-ies) presents experimental data on differential scanning calorimetry of the cholesteryl chloride and the spectra of selective light reflection that demonstrate that the optical feature observed by Planer is indeed caused by the cholesteric liquid crystalline phase of cholesteryl chloride. Thanks to the translation by Oelschlaeger, Cordova Mireles and Kitzerow, the note by Planer, originally published in German is now available in English. Trokhymchuk overviews an available literature on the early days of liquid crystal science and the role of observations made by Julius Planer. To complete, Bilyy and Lutsyk present a brief biography of the scientist, citing his research in other areas.

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