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Nanoparticle controlled soft complex structures with topological defects

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14. ABSTRACT The goal of the project was to investigate new complex multifunctional materials and morphologies by combining anisotropic soft materials possessing topological defects (TDs) with nanoparticles (NPs) and to develop appropriate mesoscopic models describing their behavior. In these structures we used topological defects as trapping centers of appropriate NPs by exploiting the so called Defect Core Replacement (DCR) mechanism. As representative soft materials we have mostly used thermotropic liquid crystalline (LC) phases. The principal subtopics of our investigation were 1) geometrically driven control of number and positioning of TDs, and 2) NP driven stabilization of various LC structures and lattices of topological defects. Among other findings, we have shown that geometry of NPs plays important role in stabilizing different blue phase structures. In particular, we have shown that highly anisotropic graphene nanosheets stabilize blue phase I, while spherical CdSe NPs stabilize blue phase III. Our results prove that i) appropriately surface treated NPs could stabilize diverse lattices of topological defects, ii) minute concentrations of NPs could enhance stability range of these structures by order of magnitude. Trapped NPs could be carrier of additional material property, i.e., in our study we inserted quantum dots exhibiting photoluminescence.					
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Nanoparticle controlled soft complex structures with topological defects

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1) Summary

The goal of the project was to investigate new complex multifunctional materials and morphologies by combining anisotropic soft materials possessing topological defects (TDs) with nanoparticles (NPs) and to develop appropriate mesoscopic models describing their behavior. In these structures we used topological defects as trapping centers of appropriate NPs by exploiting the so called *Defect Core Replacement* (DCR) mechanism. As representative soft materials we have mostly used thermotropic liquid crystalline (LC) phases. The principal subtopics of our investigation were 1) geometrically driven control of number and positioning of TDs, and 2) NP driven stabilization of various LC structures and lattices of topological defects. The main results are as follows.

We have developed two dimensional ($d=2$) mesoscopic theory in terms of nematic tensor order parameter to study impact of geometry on number and position of topological defects of topological charge $m=\pm 1/2$ in thin films exhibiting orientational ordering. These systems are representatives of nematic shells or biological membranes possessing in-plane orientational ordering. We have shown that positive (negative) Gaussian curvature K attracts TDs with $m=+1/2$ ($m=-1/2$). Geometries exhibiting regions with both signs of K could trigger unbinding of additional pairs of topological defects. Therefore, interaction between K and m shows analogy with electrostatics, where the role of K and m is played by electrical field and electrical charge, respectively. Our results signal that surface curvature can be exploited to localize TDs and to produce arbitrary number of TDs. We also propose that unbinding of TDs might play important role in fission of biological membranes. Furthermore, our mesoscopic modeling suggest second order character of the phase transition into orientationally ordered LC phase on decreasing temperature from the isotropic phase in effectively two dimensional systems. For $d=3$ this transition is of 1st order. We have demonstrated the predicted dimensional-crossover driven phase behavior change by studying 12CB LC confined to controlled-pore glasses of various pore radii R . In these samples surface interaction between LC and confining matrix is weak enough which enabled us to observe the dimensional cross-over.

We have proven the efficiency of universal character of adaptive-defect-core-targeting (ADCT) mechanism - which we introduced - in stabilizing qualitatively different defect lattices in symmetry-breaking phases. The efficient trapping of TDs within lattices requires delicate balanced interaction with a gauge field (GF) exhibiting TDs of interest. It should sufficiently disrupt GF in order to locate a neighbouring TD and to direct a NP towards it. On the other hand, it should relax the interaction with GF when a NP is trapped within the core. For this purpose we have used appropriately surface functionalised CdSe quantum dots (QDs) immersed in chiral liquid crystals. We were the first to show that these NPs have potential to efficiently stabilize lattices of line disclinations (in blue phase III) as well as line dislocations (in smectic A twist grain boundary phase). Furthermore, we have shown that geometry of NPs plays important role in stabilizing different blue phase structures. In particular, we have shown that highly anisotropic graphene nanosheets stabilize blue phase I, while spherical CdSe NPs stabilize blue phase III. Our results prove that i) appropriately surface treated NPs could stabilize diverse lattices of topological defects, ii) minute concentrations of NPs could enhance stability range of these structures by order of magnitude. Trapped NPs could be carrier of additional material property, i.e., in our study we inserted quantum dots exhibiting photoluminescence. We have also studied theoretically structural properties in mixtures of NPs and nematic LCs, where NPs impose random-field-type behavior. We have shown that the NP driven disorder introduces into system domain-type pattern characterized by a single coherence length ξ . The latter obeys the universal Imry-Ma-Larkin scaling law $\xi \propto D^{-2/(4-d)}$, where D measures the disorder strength.

Results of the project have been so far presented in several invited lectures and eight papers: 1) *Int. Rev. Bio. Chem.* **3**, 157-162 (2012); 2) *Int. J. Nanomedicine* **8**, 677-687(2013); 3) *Fluid Phase Equilib.* **351**, 87-93 (2013); 4) *Soft Matter* **9**, 3956-3964 (2013); 5) *Adv. Cond. Matter Phys.* **2013**, 505219-1-505219-10 (2013); 6) *J. Phys.: Condens. Matter, Special Issue on Condensed matter analogues of cosmology* **25**, 404201-1-404201-10, (2013); 7) *Appl. Opt.* **52**, E47-E52 (2013); 8) *Appl. Phys. Lett.* **103**, 143116 (2013))

2) Introduction

Functional soft materials by themselves cover a broad multidisciplinary research area [1]. Recent studies reveal that by combining unique properties of soft materials and nanoparticles (NPs) new hybrid materials with exceptional properties can be synthesized [1,2]. These features are promising to open doors to a plethora of new devices and applications. With this respect there is a need to develop robust synthesis strategies enabling to produce new soft complex nanocomposites with tunable functionality and/or exceptional material properties. The main goal of the project was to explore innovative synthesis strategies in forming new soft nanocomposites by exploiting universal and relatively well developed physics of topological defects [3] (TDs). Furthermore, exploitation of complex interactions between NPs and TDs were of interest and role of TDs in biological membranes [4].

As basic working material we select soft materials exploiting their i) strong response to even weak external stimuli, ii) optical anisotropy and transparency, iii) their selforganizing capabilities. As soft materials [5] we consider various liquid crystals (LCs) and biological membranes. We combined these materials with various nanoparticles. The latter (i) either contribute to the desired, controllable properties of the resulting hybrid material with potential application interest, or (ii) stabilise desired pattern which is otherwise unstable, metastable or exist in a narrow temperature interval.

Recent studies reveal that appropriately surface decorated NPs could be trapped within cores of topological defects in various LC phases [6,7]. Furthermore, appropriate NPs could substantially increase (by orders of magnitude) the stability range of relevant defect lattices due to the universal *Defect Core Replacement* (DCR) mechanism [7]. For example, due to this mechanism magnetic vortices of Abrikosov superconducting lattice of defects are efficiently pinned to impurities [8]. Efficient trapping mechanisms require i) existence of long range forces in the system to direct NPs to defects and ii) energetically favored NP-defect coexistence. It is important to identify key parameters supporting efficient “fishing” of NPs to various topological defects. In addition, trapped NPs could be used as “Trojan horses” to introduce additional quality&functionality into a system. For example, NPs could be carriers of magnetic/electric dipoles, or some other extraordinary material property (anomalous anisotropy of carbon-type nano-objects, quantum dot luminescence, NPs displaying plasmonic excitations...) which the LC matrix does not possess. Combination of new effective material properties with tunable NP-geometrical template promises to yield new complex systems with exotic properties opening pathways to various new applications.

Therefore, by controlling TDs one could indirectly control positioning of trapped NPs. As basic defect network templates one could exploit LC phases exhibiting regular lattices of topological defects. Examples of such naturally occurring structures in LCs are various blue phases [6] and twist grain boundary phases [9], exhibiting lattices of defects in orientational and translational LC ordering, respectively. In these cases defect lattices are formed due to an inherent LC material property: chirality. However, such structures could be imposed also geometrically or via appropriate external electric or magnetic fields. For example, simple 2D XY models [10], which were originally developed to study magnetic phenomena, suggest that interaction between Gaussian curvature K and topological defects is similar to the interaction between electric field and electric charges. Furthermore, strong enough local curvatures in regions separating local structures with opposite sign of K could give rise to defect pair unbinding [10].

Interactions of TDs on colloidal liquid crystalline shells with appropriate nanobinders could also open gates to form scaled crystals [11] at μm scale, also suggesting numerous application possibilities. These shells inevitably possess topological defects in LC orientational ordering due to topological reasons. Furthermore, the number of defects, their type and spatial distribution could be controlled by the geometry [10] of the shell or other control parameters. It was recently proposed to disperse appropriately coated shells within isotropic media including appropriate nano-sized binders [11]. The

latter would anchor to defect sites and in this manner organize shells into regular crystal superstructures. This research topic is still in its infancy. At this stage only various defect structures in relatively simple geometries (spherical and elliptical) have been analyzed [12,13]. There is a need to find simple ways to control sensitively the valence of LC shells and in particular to develop strategies to assemble them in crystal structures of desired symmetry. This would allow tailoring specific optical dispersion relations or other physical property of interest.

Furthermore, TDs in membranes exhibiting orientational order are relatively weakly explored [14]. Changes in membrane shapes are linked with several cellular processes of vital biological importance [15]. Structural changes might be provoked by varying external conditions (temperature, pressure, concentration...), changes in effective elasticity by adhering nanoparticles or colloids, or by some other means. A rich variety of further membrane shape changes could be triggered in the presence of various NPs which exhibit strong interactions with topological defects.

These are the topics that we addressed within the project.

3) Methods, Assumptions, and Procedures

The research consisted of sample preparations, experimental measurements, theoretical modeling and numerical simulations. As LCs we used either chiral (CE8, CE6) or relatively flexible (12CB) LCs. We used different NPs of various geometries and characteristic sizes. Most measurements were done using CdSe quantum dots, MoS₂ platelet like NPs and graphene sheets. Surface treatment of NPs was carried out by our collaborators at *National Centre for Scientific Research "Demokritos"*, Athens, Greece. Samples were probed by optical microscopy, high precision calorimetry or x-ray scattering (at ELETTRA Synchrotron, Italy). Modeling was performed at a mesoscopic scale. Corresponding equilibrium equations were solved numerically. Some simulations were performed also using lattice semi-microscopic description and Brownian Molecular Dynamics approach. Below we describe in more detail our approaches.

A) Experimental Methods

i) High-resolution adiabatic scanning calorimetry.

The calorimetric apparatus is home-made and fully-computerized. It consists of four stages, with the inner one composed of the sample-cell and three surrounding shields, with the air among them being vacuum-pumped. The capability of adiabatic scanning calorimetry for simultaneous and accurate determination of heat capacity and enthalpy, enables high-resolution studies of phase transitions and critical phenomena. The exceptional temperature stability of $\pm 50 \mu\text{K}$ and the slow scanning rates bring the sample close to the real thermal equilibrium, allowing the precise determination of phase diagrams. The heat capacity of the empty cell was measured in a separate control experiment and it was subtracted in order to derive the net C_p of the sample.

ii) Polarizing optical microscopy.

The samples were placed within 1cm x 1cm glass slides. For homeotropic cells, the glass surfaces were coated with octadecyl dimethyl (3-trimethoxysilylpropyl)ammonium chloride (ABCR GmbH), in order to obtain strong perpendicular surface anchoring of the LC molecules on a chemisorbed DMOAP monolayer. For planar cells, a thin layer of polyimide (PI-2555, NISSAN Chemicals) spin coated on the surface of the glasses. A velvet cloth was used for unidirectional rubbing on polyimide for achievement of a planar alignment on the glasses. A uniform cell thickness of 5 μm was obtained by using mylar spacers and the thickness was determined through transmission spectra using a fiber optic spectrometer (Ocean Optic, USB-2000). The cells were typically heated to the isotropic phase and filled with samples. The temperature was slowly changed by means of an Instec, STC 200 controller. The textures were observed under a polarizing optical microscope (Nikon, Eclipse E600 POL), using a color camera (PL-A742, Pixelink).

iii) X-ray measurements

The X-ray measurements were performed in the Austrian Beamline, located at ELETTRA Synchrotron (Trieste, Italy). An asymmetric-cut, double-crystal monochromator and a double-focusing toroidal mirror were used to produce a focused X-ray beam of 8 keV. Samples were mounted in capillary tubes (Hingelberg Mark capillaries, no. 14) and temperature was controlled by an in-house-built heating stage combined with a water bath (Huber Unistat). No orientation was imposed on the sample for X-ray measurements.

B) Theoretical approaches

i) Mesoscopic modeling of ordering in effectively two-dimensional films

To study orientational ordering in thin films we used phenomenological Landau-de Gennes - type model where the degree of ordering is expressed with the two-dimensional tensor order parameter Q .

Local curvature was described with the curvature tensor $\mathbf{C}$. We expressed the free energy of systems in terms of $\mathbf{Q}$ and $\mathbf{C}$ where only essential symmetry allowed terms were included to identify key mechanism affecting position and number of TDs. In studying nematic shells shape of shells was rigidly imposed. In studying membranes we assumed that $\mathbf{C}$ is primary and $\mathbf{Q}$ secondary parameter of the model. Therefore, we assume that a membrane shape is primarily dictated by the curvature tensor. We restricted to shapes exhibiting axial symmetry. Different LC configurations were obtained numerically by solving corresponding Euler-Lagrange equilibrium equations.

ii) Semi-mesoscopic modelling

To study impact of NP-induced disorder we used lattice approach with Lebwohl-Lasher-type interactions. We assumed that NPs of concentration p (below percolation threshold) were randomly spatially distributed. We assumed that they locally enforce randomly chosen frozen orientations with coupling strength W . Rod-like LC molecules and NPs were placed in cubic three dimensional lattice. The total interaction of systems was given as the sum of pairwise interactions over the lattice sites. Dynamics of systems was followed using standard Brownian Molecular Dynamic approach.

4) Results and Discussion

Our investigations consisted of two main work packages:

WP1: Geometrically driven control of number and positioning of TDs,

WP2: NP driven stabilization of various structures and lattices of topological defects.

Within WP1 we studied theoretically and numerically impact of curvature on position and number of TDs in the relevant gauge field. Our study reveals how one can geometrically manipulate TDs. We also performed experimental studies to test phase behavior change in effectively two-dimensional systems which is predicted by our modeling.

In WP2 we study experimentally and theoretically trapping efficiency of appropriately surface decorated NPs within networks of topological defects focusing. In addition we have studied theoretically and numerically impact of NP induced random-field-type of disorder on structural properties. In these studies we focused mostly on universal behavior, where we draw analogies with magnetism and also other fields of science.

WP1: Geometrically driven control of number and positioning of TDs

We have developed two-dimensional Landau-de Gennes tensorial formalism to study phase and structural properties in effectively two dimensional systems exhibiting orientational ordering [16,17]. The latter is determined by tensor order parameter, consisting of amplitude λ and gauge field component. In our formalism defects appear in the gauge field wherever a scalar order parameter λ vanishes. Our focus has been to understand impact of curvature on number and position of topological defect. Using our model we have calculated numerically equilibrium configurations in thin films of nematic liquid crystal (nematic shells) deposited on the boundary of colloidal particles of arbitrary shape enforcing a degenerate tangential anchoring on the nematic molecules. Such systems to some extent also mimic biological membranes exhibiting in-plane orientational ordering.

Our study [16,17] reveals that position and number of TDs can be strongly affected by Gaussian curvature of oriented films. In cases studied defects with winding numbers $m = \pm 1/2$ appear, where we refer to TDs with $m = 1/2$ as *defects* and with $m = -1/2$ as *antidefects*. It is demonstrated that *defects* are attracted to regions with maximal positive Gaussian curvature K . On the contrary *antidefects* are attracted to membrane regions exhibiting minimal negative value of K . We show on film structures exhibiting spherical topology that coexistence of regions with $K > 0$ and $K < 0$ might trigger pairs *defect-antidefect* for strong enough local film curvatures. We determined critical conditions [17] for this event for a demonstrative case.

Figure 1 illustrates impact of curvature on number and position of TDs. Three different nematic shell (or membrane) shapes are plotted where degree of ordering λ is superimposed. Regions with white color exhibit degree of ordering comparable to bulk ordering λ_b (in absence of curvature). Within colored regions the degree of orientational ordering is essentially melted. These regions reveal existence of topological defects (TDs).

Relative position of defects, their number and core structure is better visualized by plotting degree of ordering in the (s, φ) plane of surfaces exhibiting spherical topology. Here φ is the azimuthal angle and s measures a distance along meridians (the upper point in structures correspond to $s=0$ and the lower point to the length s_0). Within a spherical membrane (Figs. 1a, 2a) there are four TDs exhibiting topological charge $m=1/2$. These defects repeal each other and consequently they fall at the vertices of a tetrahedron in order to maximize their mutual separation.

Structure shown in Fig.1b and Fig.1c exhibit spatially dependent Gaussian curvature K . The latter has similar impact on topological defects as electric field on electric charges. In Fig. 1b the central region exhibits $K < 0$. Consequently, TDs bearing $m=1/2 > 0$ are pushed towards the poles of

membranes. In structure shown in Fig. 1c elastic distortions in region where $K < 0$ is strong enough to trigger unbinding of TDs. Two additional pairs of defects appear, where each pair consist of TDs bearing $m=1/2$ and $m=-1/2$. Defects with $m=1/2$ tend to assemble in the region exhibiting maximal value of K . Their relative position compromises this tendency and their mutual repulsion. On the other hand defects with $m=-1/2$ assemble at the neck of the structure shown in Fig. 1c, which exhibits most negative value of K .

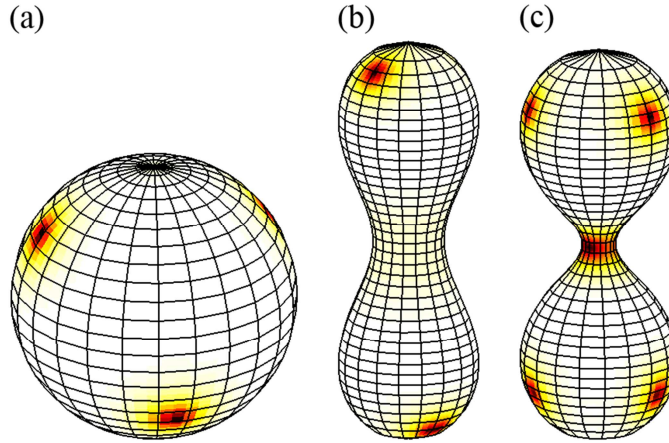


Figure 1. Two-dimensional plot of λ superimposed on thin film shapes possessing spherical topology. Colored points reveal existence of topological defects.

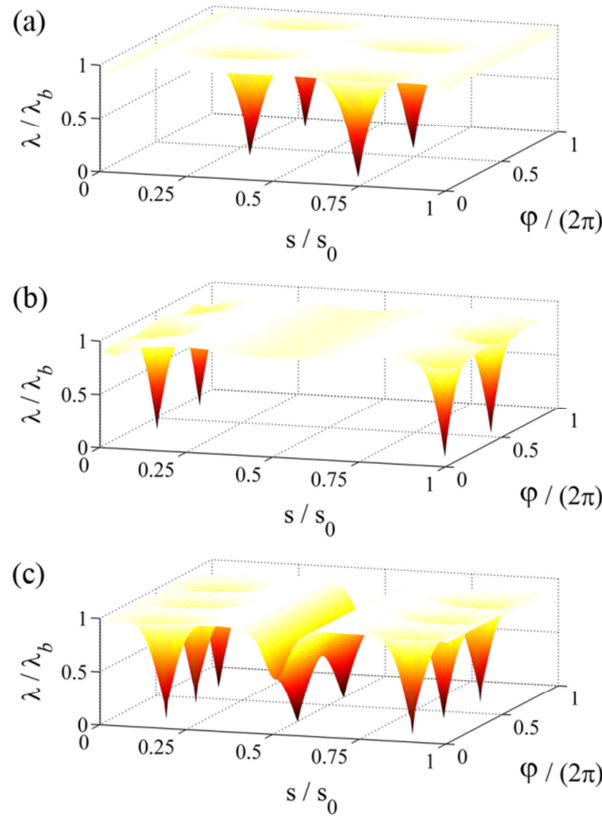


Figure 2. Two-dimensional plot of λ in the (ϕ, s) plane. There are four topological defects in (a) and (b) and eight in (c).

We claim that observed accumulation of *antidefects* at the membrane necks might play important role in membrane fission processes [17]. For example, membrane budding often leads to formation and release of microvesicles. The latter might play important role in long distance cell-cell communication owing to their ability to move with body fluids. Furthermore, our results represent a pioneering step towards formation of soft scaled crystals [11]. Namely, suspensions of nematic shells and appropriate nano-sized binders could be exploited as tunable scaled crystals and consequently tunable band-gap materials. In shells topological defects correspond to valence in real atoms.

Note further that our tensorial model [16,17] describing ordering in thin LC films suggests that phase transition into ordered phase should change from 1st order in $d=3$ to 2nd order character in $d=2$. Our experiments [18] of LCs confined to CPG matrices of different characteristic pore radii R confirm this universal prediction. On decreasing R the effective system dimensionality d_{eff} decreases and the latent heat L gradually vanishes, see figure 3. In order to observe theoretically predicted dimensional crossover one needs samples where noncritical surface interactions play secondary role. We have shown that for this purpose relatively flexible LC molecules (12CB) are needed.

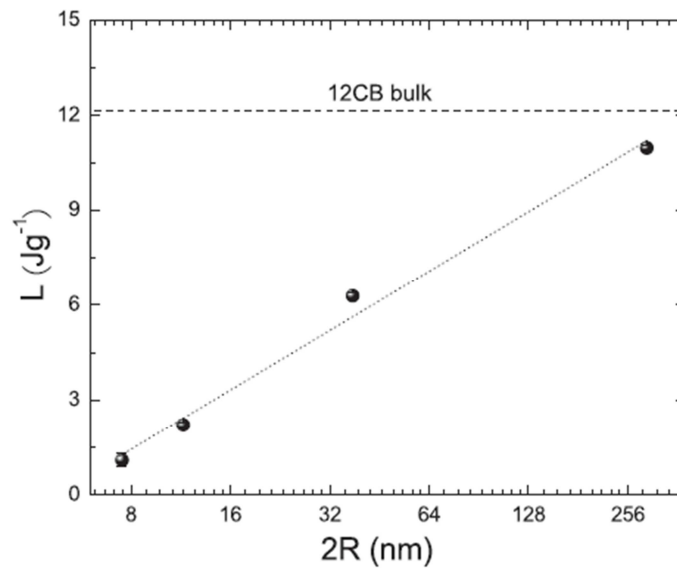


Figure 3. Latent heat L as a function of the pore diameter $2R$ for 12CB liquid crystals confined to porous glasses. The dotted line serves as guide to the eye and the dashed line represents the latent value for the bulk LC. The diagram reveals that on decreasing R the phase transition character tends to change.

WP2: NP driven stabilization of various structures and lattices of topological defects

We studied [19-21] experimentally and theoretically different modulated structures of topological defects stabilized by adaptive targeting nanoparticles. In our experiments we used as NPs magic quantum dots CdSe [19] exhibiting size dependent photoluminescence, platelet-like shaped MoS₂ NPS [20], and graphene sheets [21]. As host we used chiral LCs (CE6, CE8).

By using appropriately surface decorated spherical CdSe NPs we succeeded [19] to stabilize LC structures exhibiting qualitatively different lattices of topological defects. These NPs are efficient to stabilize blue phase III hosting lattice of line disclinations (TDs in orientational degree of freedom). In addition they stabilize also smectic A twist-grain boundary phase which possesses lattice of screw dislocations (TDs in translational degree of freedom). Note that the latter phase represents LC analogue of the Shubnikov phase in type-II superconductors [9]. We were the first to identify a universal adaptive-defect-core-targeting (ADCT) mechanism [19]. This mechanism enables the effective reduction of the energetically-costly, singular defect core volume, while the surrounding phase ordering remains relatively weakly affected.

In figure 4 we present main ideas of the proposed ADCT mechanism. In (A) we sketch surface-treated CdSe nanoparticles (top left) which tend to be assembled within screw dislocations at the grain boundaries (GBs) separating the twisting smectic slabs (bottom). A blow-up of the TGB_A unit cell is presented at the top right. Because NPs partially replace energetically stable defect core structure stability of structures hosting TDs are increased. In (B) and (C) the adaptive character of CdSe NPs, enabled by the flexible surface chains that also prevent phase separation, is depicted. The NPs accommodate with the average local orientational order of the qualitatively different disclination lines (B) and smectic screw dislocations (C), that characterize the BPs and the TGBs, respectively. The impact of NPs on smectic layers is relative weak because they reside in regions where the translational order is essentially melted.

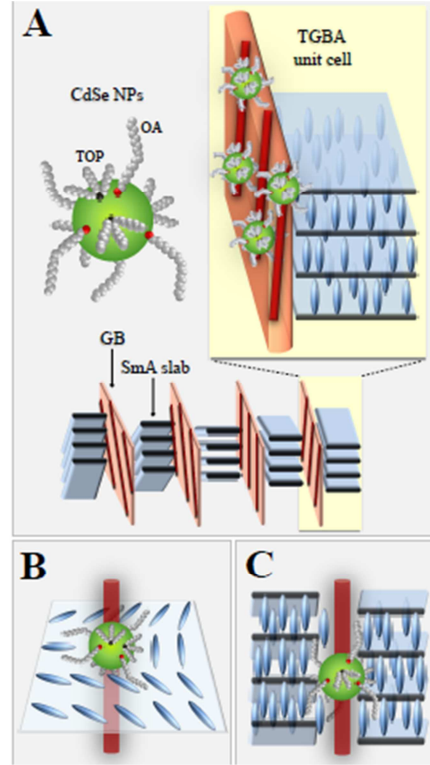


Figure 4. Adaptive NPs tend to assemble at cores of TDs. In (A) we plot CdSe NPs decorated with flexible chains (top left). Bottom part of figure A illustrates TGBA phase consisting of lattices of screw dislocations located within grain boundaries (GB), which separate blocks with smectic A ordering. At the top right we present a blow-up of TGBA unit cell in which we illustrate assembling of NPs at cores of defects. In (B) and (C) we present adaptive character of NPs which is enabled by attached flexible chains. In cases shown NPs adapt either to surrounding core structure of nematic disclination (left) and smectic dislocation (right). Consequently, they relatively weakly perturb surrounding LC structure. Because they decrease singular volume of dislocation they efficiently decrease their condensation penalty which is required topologically.

In Figure 5 we present main results of our study. We show increased temperature phase stability of blue phase III (BPIII) and twists grain boundary A (TGBA) phase on increasing mass concentration x of NPs. One sees that for $x=0$ the stability range of BPIII phase is confined to a relatively narrow temperature interval and TGBA phase is absent. Presence of appropriately surface functionalised NPs stabilizes TGBA phase. Furthermore, by increasing x the stability range of BPIII and TGBA phases exhibiting topological line defects is dramatically increased.

Study presented above shows that spherical NPs could stabilize BPIII phase [19]. Furthermore, we demonstrate that surface-functionalized graphene nanosheets [21] stabilize BPI phase, which has different organization of defect lattice. Our measurements demonstrate that the resulting soft

nanocomposite exhibits an increased BPI temperature stability even for a minute concentration of dispersed graphene. Therefore, different geometries of NPs could be exploited to stabilize different organisations of defect lattices.

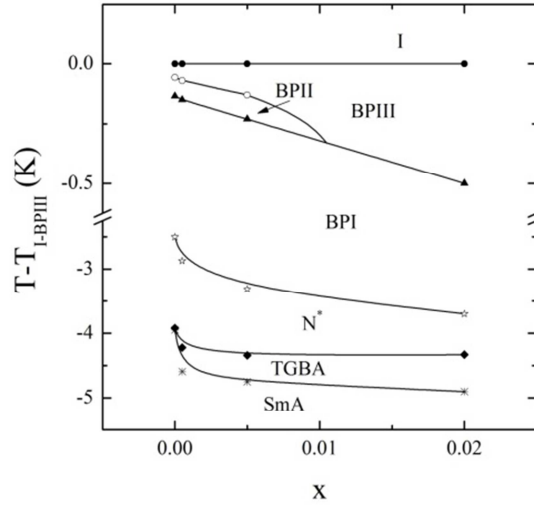


Figure 5. In mixtures of CE6 LC and CdSe NPs (quantum dots) we succeeded to substantially increase stability of BPIII phase exhibiting a lattice of disclinations (TDs in orientational ordering) and TGBA phase exhibiting lattice of screw dislocations (TDs in translational ordering).

We also performed intensive simulations in order to test impact of NPs induced disorder [22,23] on LC structural behavior. Well known examples of such systems are mixtures of LCs and spherular aerosol [24] NPs. We focus on the impact of the samples history on the universal behavior. The obtained results are of interest for every randomly perturbed system exhibiting a continuous symmetry-breaking phase transition in case of relatively weak disorder. We studied impact of history of samples on key macroscopic characteristics of perturbed LC structures. Simulations were carried out for temperature-quenched and field-quenched histories (TQH and FQH respectively), as well as for temperature-annealed histories. The first two of these limits represent extreme histories encountered in typical experimental studies. Using long-time averages for equilibrated systems, we calculate orientational order parameters and two-point correlation functions. Finite size-scaling was used to determine the range of the orientational ordering, as a function of LC-NP coupling strength W and concentration p of NPs. Numerical results support assumption that history of samples plays significant role. For TQH systems pass from long-range-order (LRO), via quasi-long-range (QLRO) towards short-range-order (SRO) regime on increasing coupling strength W for a given concentration p . On the contrary for FQH the system exhibits only LRO and QLRO within the investigated window of parametrs. We found that even in QLRO regime a domain-type structural pattern is also inherently present as already suggested in magnetic systems. Measured different range of order suggests that structural crossover between neighboring domains is on average smoother in the QLRO regime with respect to the SRO regime. For both histories in both QLRO and SRO regime estimated characteristic domain sizes ξ are comparable. In weak coupling regime universal Larkin-Imry-Ma [25] scaling $\xi \propto D^{-2/(4-d)}$ hold true, where D measures effective disorder strength. We have also shown that one could exploit such system to store information by exposing a system temporarily to various strengths of external electric or magnetic external field. In summary, our simulations explain why different experiments in previous studies often yield contradiction results on range of order. The reason behind this were different histories of samples.

To conclude, our study demonstrates that the ADCT mechanism-driven trapping of appropriate NPs could stabilize diverse structures exhibiting topological defects. This is of great importance

towards the controlled assembly of nanoparticles in soft, anisotropic media. For example, the trapped NPs can be exploited as *functionality-conveying agents*, as demonstrated in the case of photoluminescence of CdSe quantum dots. Moreover, the trapped-NP triggered nucleation and stabilization of structures that exhibit topological defects visible by means of optical microscopy, could be exploited for the development of sensitive detectors. Our simulations also show that presence of NPs could enforce strong memory effects if they enforce a kind of random-field type disorder. The resulting behavior shows pronounced universal behavior because the key ingredients of such systems is continuous symmetry breaking. Our results suggests that appropriate mixtures of NPs and LCs could also be exploited as memory devices.

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6) List of Symbols, Abbreviations, and Acronyms

ADCT :	Adaptive-defect-core-targeting	K :	Gaussian curvature
BP :	Blue phase	m :	Topological charge
CPG :	Controlled pore glass	$\mathbf{C}$:	Curvature tensor
DCR :	Defect-core-replacement	$\mathbf{Q}$:	Nematic tensor order parameter
FQH :	Field-quenched history	λ :	Scalar nematic order parameter
GB :	Grain boundary	ξ :	Domain size
GF :	Gauge field	d :	Space dimensionality
LC :	Liquid crystal	D :	Disorder strength
NP :	Nanoparticles	W :	NP-LC Coupling strength
QD :	Quantum dots	x :	Mass concentration on nanoparticles
TD :	Topological defects	p :	Volume concentration on nanoparticles
TGB :	Twist grain boundary		
TGBA :	Twist grain boundary A		
TQH :	Temperature-quenched history		
WP1 :	Work package 1		
WP2 :	Work package 2		