

COLLOIDAL INTERACTIONS AND NOVEL COLLOIDAL STRUCTURES IN THIN NEMATIC LAYERS

Doctoral Dissertation
Jožef Stefan International Postgraduate School
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Supervisor: Prof. Dr. Igor Muševič, Jožef Stefan Institute, Ljubljana, Slovenia

Evaluation Board:

Prof. Dr. Zdravko Kutnjak, *Chairman*, Jožef Stefan Institute, Ljubljana, Slovenia

Prof. Dr. Slobodan Žumer, *Member*, University of Ljubljana, Ljubljana, Slovenia

Prof. Dr. Samo Kralj, *Member*, University of Maribor, Maribor, Slovenia

Uroš Tkalec

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MEDDELČNE INTERAKCIJE IN NOVE KOLOIDNE STRUKTURE V TANKIH NEMATSKIH PLASTEh

Doktorska disertacija

Supervisor: Prof. Dr. Igor Muševič

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MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA
JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL
Ljubljana, Slovenia



I stand at a seashore, alone, and start to think...
There are the rushing waves...
Mountains... of molecules,
each stupidly minding its own business...
trillions apart...
yet forming white surf in unison.
Ages on ages...
before any eyes could see...
year after year thunderously pounding the shore
as now.
For whom, for what?
On a dead planet, with no life to entertain.
Never at rest...
tortured by energy wasted prodigiously by the
sun... poured into space.
A mite makes the sea roar.
Deep in the sea, all molecules repeat the patterns
of one another till complex new ones are formed.
They make others like themselves...
And a new dance starts.
Growing in size and complexity...
living things, masses of atoms, DNA, protein...
Dancing a pattern ever more intricate.
Out of the cradle onto the dry land...
Here it is standing...
atoms with consciousness...
matter with curiosity.
Stands at the sea...
Wondering I...
a universe of atoms
an atom in the universe.

RICHARD P. FEYNMAN, *Science and Ideas*,
edited by A. B. Arons (Prentice-Hall, 1964).

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Abstract

The thesis presents experimental studies of colloidal interactions and novel colloidal structures in confined nematic liquid crystal using optical tweezers. Liquid crystal colloids are a novel class of composite materials with well-controlled periodic structures in the nanometer and micrometer ranges. Moreover, they also possess novel mechanical, optical and rheological properties, which makes them potentially interesting for applications in photonics, electro-optics, sensors and metamaterials. Likewise, they are promising to play an important role in the future development of self-assembling soft matter systems.

This work is primarily focused on two-dimensional assembly of colloidal inclusions in thin nematic layers. The inclusions induce distortions and topological defects, characterized by dipolar and quadrupolar symmetry of the molecular orientation field in the continuous liquid crystalline matrix. These distortions can mediate elastic interactions among dispersed particles and direct their spatial ordering into variety of self-assembled colloidal architectures. It has been shown that regular two-dimensional nematic colloidal crystals of elastic dipoles and quadrupoles can be assembled using optical tweezers and stabilized by nematic elasticity. The assembly process was to some extent automated by the application of external electric field, which enabled the massive and directed transport of colloidal particles on macroscopic scale. Furthermore, a novel binding mechanism has been demonstrated, where colloidal particles are entangled by delocalized disclination lines. Nematic braids, formed by such disclinations, stabilize new topological objects and entrap particles in a complex manner.

The main results of the thesis are organized in three independent sections. Firstly, we present the experimental analysis of elastic distortions around rod-like particles in homogeneous nematic layers and demonstrate that interparticle forces do not crucially depend on the shape of inclusions. Secondly, we show that the chiral ordering of the underlying complex fluid strongly influences defect formation and colloidal interactions. Escaped hyperbolic defect rings with multiple configurations are energetically stabilized by non-uniform director geometry of a twisted nematic cell. Here, chiral dimers and novel two-dimensional colloidal crystals of pure and mixed chirality, intercalated with a lattice of escaped defect loops, are reported. Thirdly, we have observed that chiral nematic field reverses the stability and metastability of entangled and non-entangled colloidal structures. This finding allowed us to create reconfigurable entangled two-dimensional colloidal clusters and periodic crystals with an enormous number of conformations. Such conformations possess topological structure of various knots and links, formed by topological frustrations of the liquid crystal orientation field. They have been precisely analyzed applying the mathematical theory of knots and we believe that this work opens a new link between colloidal science and knot theory. Moreover, we anticipate that such knotted patterns may also find use as a model system for studying knotted conformations in confined and chiral environment, as well as light-addressed surface memory or as topological target for the scaffolding of dispersed biopolymers.

Keywords: optical tweezers, colloids, nematic liquid crystal, self-assembly, phase transitions, topological defects, entanglement, knot theory.

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Povzetek

Doktorsko delo obravnava raziskave meddelčnih interakcij in sestavljanje novih koloidnih struktur v ograjenem nematskem tekočem kristalu z optično pinceto. Tekočekristalni koloidi so nova vrsta kompozitnih materialov z dobro definiranimi periodičnimi strukturami v nanometrskem oziroma mikrometrskem območju. Imajo tudi možnost uravnavanja mehanskih, optičnih in reoloških lastnosti. Zaradi tega so zanimivi za uporabo v fotoniki, elektro-optiki, senzorjih in metamaterialih. Prav tako gre pričakovati, da bodo odigrali pomembno vlogo pri razvoju samosestavljaljivih mehkih sistemov.

Pričujoče delo je primarno posvečeno sestavljanju dvodimenzionalnih koloidnih struktur v tankih nematskih plasteh. Dispergirani koloidni delci s svojo prisotnostjo spremenijo lokalno urejenost tekočega kristala in povzročijo nastanek topoloških defektov z lokalno dipolno oziroma kvadrupolno simetrijo okoliškega molekularnega polja. Nastale motnje nematske urejenosti posredujejo elastične sile med dispergiranimi delci in vplivajo na njihovo prostorsko razporeditev. Odkritje in razumevanje tega mehanizma je bilo ključnega pomena, saj je sprožilo razburljivo iskanje samosestavljaljivih struktur v nematskih koloidnih disperzijah. S sodelavci smo pojasnili sestavljanje stabilnih dvodimenzionalnih nematskih koloidnih kristalov z dipolno oziroma kvadrupolno simetrijo in kot vezavni mehanizem identificirali elastičnost tekočega kristala. Postopek sestavljanja je bil delno avtomatiziran z uporabo zunanega električnega polja, ki omogoča masovni transport delcev na makroskopskem nivoju. V nadaljevanju je bil odkrit nov vezavni mehanizem, pri katerem interakcije med koloidnimi delci v nematskem tekočem kristalu posredujejo delokalizirane defektne linije. Z natančno manipulacijo defektnih linij in koloidnih delcev izdelamo nematske pletenine, ki predstavljajo nov tip topološko stabilnih objektov.

Glavni rezultati doktorskega dela so razdeljeni v tri neodvisne sklope. Najprej smo analizirali topološke lastnosti tekočega kristala v okolici mikropalčk in pokazali, da oblika delcev nima bistvenega vpliva na tip meddelčnih interakcij. Nato smo pokazali, da kiralno nematsko polje močno vpliva na nastanek topoloških defektov in posledično omogoča nov način meddelčnih interakcij. V geometriji zvojne nematske celice smo sestavili koloidne pare s pobeglimi hiperboličnimi defektnimi obroči in dvodimenzionalne koloidne kristale s poljubno ročnostjo. Opazili smo, da kiralno nematsko polje dodatno stabilizira prepletene koloidne strukture in omogoča izdelavo prepletenih dvodimenzionalnih nematskih koloidnih kristalov. Te vrste nematskih pletenin so še posebej zanimive, saj smo z njimi ustvarili edinstveno eksperimentalno realizacijo topoloških objektov, ki jih obravnava matematična teorija vozlov. Rezultati predstavljajo novo paradigmo v znanosti o koloidih in napovedujejo uporabo zavozlanih topoloških vzorcev na področju modeliranja konfiniranih elastičnih filamentov, svetlobno občutljivih spominskih celic ter izdelavi topoloških tarč za urejanje dispergiranih polimerov.

Ključne besede: optična pinceta, koloidi, nematski tekoči kristal, samosestavljanje, fazni prehodi, topološki defekti, prepletenost, teorija vozlov.

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Symbols and Abbreviations

PHYSICAL QUANTITY	DESCRIPTION	SI UNIT
a, b, c	unit cell parameters	m
$\mathbf{B}$	magnetic flux density	T
d	diameter	m
D	self-diffusion coefficient	m ² /s
$\mathbf{D}$	electric flux density	C/m ²
$\mathbf{E}$	electric field strength	V/m
ϵ	dielectric permittivity	F/m
η	viscosity	kg/ms
f	free energy density	J/m ³
F	free energy	J
$\mathbf{F}$	force	N
γ	viscous drag coefficient	kg/s
h	sample thickness	m
$\mathbf{H}$	magnetic field strength	A/m
I	intensity	cd
k	trap stiffness	N/m
$K, K_{11}, K_{13}, K_{22}, K_{24}, K_{33}$	Frank elastic constants	N
L_1, L_2, L_3	basic elastic constants	N
λ	wavelength	m
m	mass	kg
ω, ν	frequency	Hz
P	power	W
$\mathbf{P}$	electric polarization	C/m
Q	latent heat	J/K
r, R	radius/distance, size	m
S	entropy	J/K
T	temperature	K
t, τ	time, self-diffusion time	s
$\alpha, \beta, \gamma, \theta, \phi, \Omega$	angle	degree
U	potential	J
ξ_E	electric coherence length	m
ξ_N	nematic correlation length	m
ξ_S	surface extrapolation length	m
v	velocity	m/s
W_e	surface anchoring strength	J/m ²

PHYSICAL CONSTANT	DESCRIPTION	VALUE AND SI UNIT
c_0	speed of light	$\approx 3 \cdot 10^8$ m/s
ϵ_0	dielectric constant	$8.854 \cdot 10^{-12}$ C ² m/J
k_B	Boltzmann constant	$1.38 \cdot 10^{-23}$ J/K
μ_0	magnetic constant	$4\pi \cdot 10^{-7}$ H/m
π	mathematical constant	≈ 3.14159

SYMBOL	DESCRIPTION
$\mathcal{B}$	biaxiality
δ_{ij}	Kronecker delta symbol
ϵ_{ijk}	Levi-Civita tensor
$\mathcal{F}$	Fourier transform
φ	phase
$\mathbb{I}$	identity matrix
k	winding number
$\mathbf{k}$	wave vector
$\mathbf{n}$	nematic director
n, N	refractive index
$\mathbf{N}$	refractive index vector
P	probability
q	topological charge
$\mathbb{Q}$	order parameter tensor
$\mathbf{r}$	position vector
S	scalar order parameter
$\mathbf{S}$	Poynting vector
$\mathbf{u}, \mathbf{e}_1, \mathbf{e}_2$	unit vector
x, y, z	Cartesian coordinates

ABBREVIATION	DESCRIPTION
AC	alternating current
AOD	acousto-optic deflectors
CCD	charge-coupled device
CMOS	complementary metal oxide semiconductor
DMOAP	N,N-dimethyl-N-octadecyl-3-aminopropyl-trimethoxysilyl chloride
DNA	deoxyribonucleic acid
Fig.	figure
fps	frames per second
ITO	indium tin oxide
LCD	liquid crystal display
LdG model	Landau-de Gennes model
min	minute
PC	personal computer
PET	polyethylene terephthalate
Ref.	reference
ROI	region of interest
rpm	revolutions per minute
SEM	scanning electron microscopy
TN	twisted nematic
UV	ultraviolet
wt%	weight percent
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
5CB	4-cyano-4'-pentyl-1,1'-biphenyl

Introduction

One of the most challenging and fascinating problems in physical science is how to encompass the wonderful variety and complexity of microscopic world into a few simple and general laws. To accomplish this aim, it is necessary to refer to notions from soft condensed matter physics, whose applications to nanotechnology mechanisms have provided remarkable successes. In spite of their diversity, soft matter systems are earthy. They occur at the room temperature and are often encountered in everyday life. Many of them, especially liquid crystals, gels, foams, polymers, membranes and granular media, can be studied with tabletop experimental equipment, which enables instantaneous and wide access to interesting physical phenomena. Liquid crystals and colloids are no exception to the above, and appear as attractive materials commonly present in the modern world, with their properties exploited for different types of applications. Recently, the constant demand for more complex material responses of both liquid crystals and colloidal dispersions has resulted in a synergy of the two fields, introducing the new composite materials, called liquid crystal colloids. The primary interest in liquid crystal colloids is related to their applications in optics, where complex anisotropic properties of liquid crystals are combined with the large response of colloidal dispersions to external fields.

1.1 Liquid crystals

All matter exists in one of several possible aggregate states, such as solid, liquid or gas, having different degree and type of positional and orientational order. In the isotropic liquid or gas phases molecules without order occupy the whole space and have no long-range positional or orientational order. The solid state can be further divided to several categories, such as glass or crystal. In a typical crystalline phase molecules or atoms possess a three-dimensional (3D) long-range positional order, while in molecular crystals a long-range orientational order also exists. The intermediate states or *mesophases* between the isotropic liquid and the crystalline phases, called *liquid crystals*, are liquid oily materials, made of highly asymmetric organic molecules that at a given temperature or molecular concentration self-organize due to anisotropic weak intermolecular interactions and thus possess long-range orientational and partial positional order. As a rule, the backbone of mesogenic molecules is rigid due to the phenyl groups, while the attached aliphatic chains are flexible. Their shape dictates the tendency of the molecules to orient in the same direction or stack into layers or columns. Such behavior causes the rise of anisotropic physical properties like optical birefringence or anisotropic viscosity, transmission of static torques, which are otherwise impossible in liquids, and the fluidity of the mesophases. Due to their unique optical properties these materials have found widespread applications in liquid crystal displays (LCDs), which have become a synonym for modern electronic display devices as they cover over 90 % of the world display market.

The most widely spread and least ordered mesophase is the *nematic* phase, characterized by long-range orientational order but no positional order [1]. The molecules tend to be parallel to a common axis that is denoted by a unit vector $\mathbf{n}$ and is called *director* [see Fig. 1.1(a)]. Whereas the director in an ordinary nematic phase has a constant direction, in a *cholesteric* or chiral

nematic phase it changes direction in a helical fashion throughout the sample. Phases with the positional order of molecules stacked into parallel layers of the same thickness are known as *smectic* liquid crystals [2]. The long-range orientational order of the molecules is therefore the central phenomenon, which makes liquid crystals unique among other states of matter. It can vary from nanometer to micrometer scale and is typically highly sensitive to various stimuli, such as temperature, electric and magnetic fields or foreign particles dissolved in the liquid crystalline matrix. In confined geometries opposing orientational ordering of different surfaces can lead to the formation of regions, where the orientation of molecules becomes undefined. In the nematic liquid crystal these defect regions exist either as lines or points.

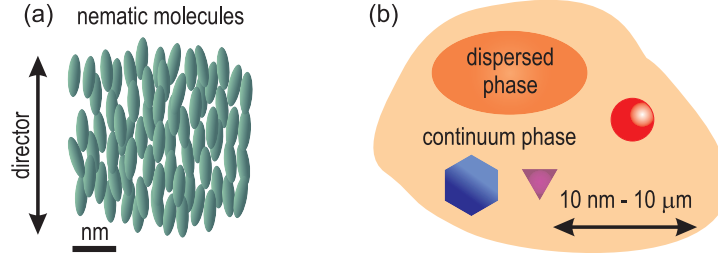


Figure 1.1: (a) A schematic presentation of nematic ordering. Nematic molecules are shown with elongated ellipsoids. Double arrow indicates the preferred average orientation of the molecules - the director. (b) Inclusions of various types and shapes within a continuum host medium forming a colloidal dispersion. Note the difference in length scales of the nematic molecular and colloidal inclusion sizes.

The first liquid crystalline compound was discovered in 1888 by the Austrian botanist Friedrich Reinitzer, who was intrigued by the observation that cholesteryl benzoate undergoes two first order phase transitions upon heating the solid compound, which was established using polarizing optical microscopy. First it melted into an unusual turbid solid state, which at higher temperature transformed into a clear liquid [3]. The intermediate turbid phase was further investigated together with German physicist Otto Lehmann and he realized that the phase was birefringent, optically anisotropic, and called it 'crystalline liquid' [4]. Observations of other similar fluids followed, with much debate on whether they were homogeneous liquid crystals, incompletely melted crystals or impure substances. In 1922 the French crystallographer Georges Friedel convincingly argued that liquid crystals represent a new state of matter, intermediate between solid crystals and ordinary liquids. Much later it was found that liquid crystals are ubiquitous in nature as phospholipid cell membranes as well as myelin, a lipid material protecting the nerves. The same holds for some concentrated DNA and protein solutions, like for instance the secretion of a spider that is used to generate silk. They are present in high strength plastics, snail slime, laundry detergents, textile fibers, components of crude oil, insect wings, eye shadow and even lipstick [5]. However, the first huge scientific interest for this state of matter rose in the 1960s and was mainly driven by the advent of technological applications of liquid crystals. Especially nematic liquid crystals have become highly attractive for fabrication of tunable optical devices such as displays, spatial light modulators and quickly responsive shutters [6,7]. The number of experiments on liquid crystalline phases increased dramatically and the theoretical explanations emerged as well [8]. The most known are Maier-Saupe microscopical theory [9] and de Gennes' phenomenological approach, using the Landau theory [10]. Particularly the work of Pierre-Gilles de Gennes is considered crucial in shaping the strategies of contemporary liquid crystal research. Since then, various numerical methods, such as Gay-Berne model [11] and Lebwohl-Lasher model [12], have been developed and followed by relaxation techniques with finite differences or finite elements and lattice Boltzmann algorithms [13,14]. With the maturation of the information display field liquid crystal materials research is undergoing a new renaissance. The aims of contemporary research are shifting away from the quest for better figures of merit in electro-optical applications towards the search for smart functional materials

[15]. Interdisciplinary links to biological and biotechnological systems, polymers, colloids and elastomer sciences have already emerged and fundamental theories of liquid crystals are percolating through many scientific communities due to the fact that liquid crystals represent a great system to study phase transitions, correlations in liquids or interactions of the liquid with surfaces. As researchers continue their endeavors, in the future we can expect both incremental advances and technological leaps to continue.

1.2 Colloids

Colloidal systems are dispersions of solid or liquid particles in a liquid host medium, where the size of inclusions ranges from few nanometers up to several micrometers [see Fig. 1.1(b)]. Their usage has been known from ancient times and they play an important role in the area of industrial applications as well as in fundamental research [16]. Among a whole variety of binary phase systems, in which one of the phases is finely dispersed in the other, one can distinguish between solid dispersions, colloidal suspensions, emulsions and foams, as well as solid and liquid aerosols. The most famous representative of ordered solid dispersions is the opal, formed from a uniform array of silica spheres which have been compressed and fused over geological timescales. However, far more common examples appear in food, with milk being the best known fat-in-water emulsion, and other solid emulsions such as butter or margarine. Some typical examples of colloidal suspensions and foams include cosmetic creams, drugs, fuel additives, ink, paints and a shaving foam. In nature, one is confronted by both the bothering and appealing side of fog, and one can look at the impressive blue-greenish color of berg lakes in the Triglav Lakes Valley, caused by light scattering from a fine dispersion of stone flower in water.

Colloidal inclusions typically interact with the host material across their surface. The transition between the macroscopic state and the colloidal state involves significant increase in the surface-to-volume ratio and can be easily visualized by sand grains. Thus, whereas 1 g of sand in the form of silica beads 1 mm in diameter possesses the modest surface area of 30 cm², the same quantity of silica divided up into superfine particles of 10 nm diameter would have an enormous total surface area of 300 m² [17]. Surfaces of inclusions can be chemically active or inactive, either charged or uncharged or can be covered with surfactants that impose different surface fields. Large diversity of colloidal systems is reflected also in a wide range of interactions that govern the behavior of colloidal materials. The surface force most frequently encountered is the van der Waals force [16]. It is of dielectric origin and is caused by the fluctuations of the charge distribution in atoms. Forces of electrostatic origin appear in colloidal dispersions with an ionizable host or with charged particles. Here, typically only a thin surface layer of colloidal particles is charged and the electrostatic potential within the host medium is exponentially screened [18]. Finally, also volume forces are important in colloidal dispersions, in external fields (electric, magnetic, gravitational) and in the ferroelectric or ferromagnetic materials.

Colloidal particles belong to useful soft matter components that have the potential to self-organize, forming complex, beautiful and regular structures. Progress in soft matter research is driven largely by the available experimental techniques and much of the work is concerned with understanding physics at the micrometer length scale. The combination of different simple soft matter systems, such as colloids, liquid crystals and polymer suspensions, and their precise micromanipulation is therefore one of the key goals in nanotechnology and materials science.

1.3 Liquid crystal colloids

During the last decade liquid crystal colloids have been attracting great interest as a novel class of composite materials involving liquid crystals [19–21]. One of the main characteristics of liquid crystal colloids that makes them highly intriguing lies in the fact that they show unusual

properties which cannot be seen in conventional colloidal systems, arising from the presence of orientational order in the host fluid inherent in liquid crystals. Colloidal particles immersed in an anisotropic liquid crystal host interact with the surrounding liquid crystal primarily through the surface anchoring [22]. Particle surfaces are usually covered with surfactants which impose strong perpendicular (homeotropic), tilted or planar orientation of the near-by liquid crystalline molecules. The surface anchoring affects the bulk orientation of the liquid crystal by generating an elastic perturbation profile of the director field. Such orientational profile usually has a dipolar or quadrupolar symmetry, while particles together with the surrounding elastic distortion and induced topological defects are often referred to as elastic dipoles or quadrupoles [21]. The elastic dipole and quadrupole are spherical particles, whose surface imposes strong homeotropic anchoring, accompanied by a hyperbolic point defect or encircled by a disclination line referred to as Saturn ring, respectively [23]. Particles imposing planar surface anchoring have quadrupolar symmetry and generate two surface defects, called boojums [24]. The symmetry and the structure of the director profile around the particles is determined by surface anchoring strength, particle size, confinement and external fields [21]. Schematics and optical micrographs in Fig. 1.2 show the dipolar and quadrupolar director configuration around a single microsphere with homeotropic surfaces and the effect of structural parameters on the director structure [21].

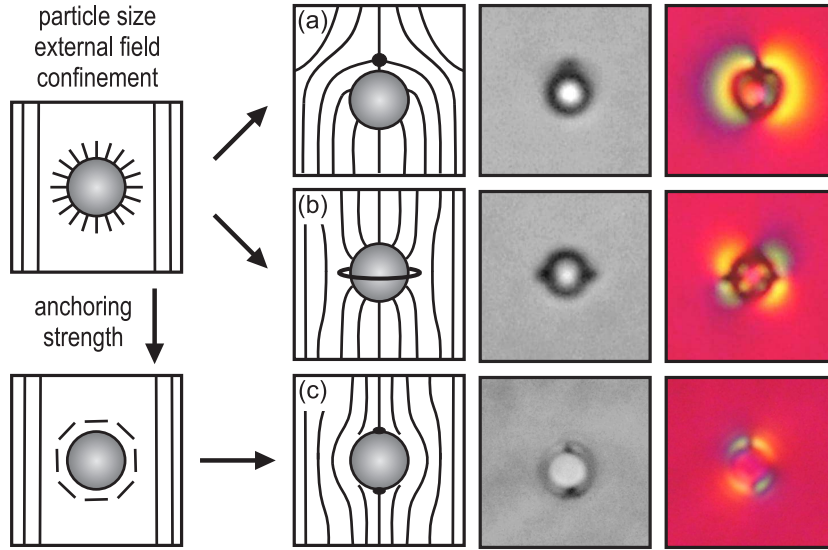


Figure 1.2: (a) Dipolar and (b,c) quadrupolar configurations of the director profile visualized by black lines around a single colloidal particle with homeotropic surface. By decreasing particle size and anchoring strength or increasing external field and confinement the dipolar structure becomes energetically less favorable and therefore transforms into the quadrupolar structure. Micrographs of a $5\ \mu\text{m}$ diameter silica particles in a thin planar layer of nematic liquid crystal, captured under depolarized and polarized light. Different colors represent different orientations of nematic molecules. Presented after Fig. 12 in Ref. [21].

Colloidal particles dispersed in a liquid crystal host are subjected to the long-range structural forces, which are imposed by the confining interfaces. These forces are of thermodynamic origin with van der Waals intermolecular interactions being their source at the molecular scale. At the particle scale, however, single molecular contributions typically smear out and liquid crystal effectively acts as an elastic medium trying to retain the orientational order of its molecules. At this scale, structural forces are therefore considered as effective elastic forces, which try to minimize the perturbation of the director field induced by inclusions. The profile of structural forces is typically highly anisotropic and is governed by the geometry of the system and the symmetry of the director. Finally, the complex interactions between inclusions in liquid crystals lead to complex relaxations processes in colloidal dispersions that give rise to rich variety of colloidal structures.

In recent years assisted and true self-assembly was reported for various liquid crystal colloidal structures [20,25,26]. The first observed nematic colloidal structures were chains of gas bubbles at the nematic-air interface used in a decoration technique to display hoops in the droplet of a cholesteric liquid crystal [8,27]. Whereas in those early experiments the nematic-air surface tension played an important role in the organization of bubbles into chains at the interface, this effects has been removed in the experiments on nematic emulsions by Poulin *et al.* [19,28]. They have shown that water droplets dispersed in the nematic liquid crystal did not coalesce, but rather formed long chains, where each droplet in a chain was separated by a topological defect, preventing their surface contact. It soon became clear that the formation of colloidal chains is due to the elastic deformation of the director field around each colloidal particle and that the mechanism, responsible for these structural forces in nematic colloids, involves sharing of regions of equal distortions. Assembly of dipolar chains at a larger length scale was realized by phase separation in the binary mixture of silicone oil and nematic liquid crystal [29]. Dipolar chain segments were further observed to build complex two-dimensional (2D) cluster aggregates [24]. Aggregates of quadrupoles in binary mixtures of a liquid crystal and isotropic dispersed phase were observed to form kinked zigzag chains [30]. The directed assembly of regular 2D nematic colloidal crystals of elastic dipoles, quadrupoles and their combination was demonstrated in the last four years [31–34], whereas shape-controlled colloidal interactions in anisotropic fluids have been reported only recently [35,36]. At the interfaces 2D hexagonal ordering of glycerol droplets and spherical colloids was observed and analyzed in great details [37–43]. In addition, particle-stabilized gels in a cholesteric liquid crystal [44,45], orientational ordering of ferromagnetic nanowires in an anisotropic fluid [46–48], combined charge and nematic stabilization of a colloidal dispersion [49], and optical tweezers measurements of interparticle forces in a nematic liquid crystal [50–53] have been reported recently.

The research in liquid crystal composites is mainly driven by the development of new optical elements, photonic structures and metamaterials [54–57]. Optical elements like 3D photonic crystals [58–60], split ring resonators [61], optical metamaterials [62–65] and negative refractive index superlenses [66–69] require a good control of the dielectric permittivity and magnetic permeability spatial profile at micrometer scale. Fortunately, the optical response of liquid crystal colloids is rather easily controlled by choosing proper particles’ sizes, surface coatings and particle arrangements [70–72], where it can be steered with external electric, magnetic or optical fields [73–75]. Moreover, in liquid crystal colloids also highly attractive self-assembly processes [31,76,77] can be applied. In contrast to colloids dispersed in an isotropic host fluid, like water, liquid crystal colloids build strong and robust structures with binding energies of several $1000 k_B T$ [78–82] for micrometer-sized particles or even $10000 k_B T$ in entangled colloidal structures [83–85]. Binding energies in water based colloids are of the order of $10 k_B T$ [86,87]. The mechanism of particle assembly by structural forces in liquid crystal colloids has also no a priori limitation for scaling down the inclusion sizes to several nanometers [88–95], which brings the possible optical application already deep in the UV regime.

1.4 Overview of the thesis

The experimental study of liquid crystal colloids is motivated by strong and continuously increasing interest in the phenomena related to the colloidal assembly. Various experimental and theoretical research groups are investigating novel colloidal interactions and self-assembly processes in liquid crystal hosts that could potentially lead to ordered colloidal structures. The future technologies and devices namely require materials with well-controlled periodic structures in micrometer and nanometer ranges, as well as with anisotropic optical properties and mechanical flexibility. Liquid crystal colloids can meet all of these requirements; they can respond to low external fields and can be manipulated by light. This makes them ideal for tunable optical applications, which however, critically depend on finding the means to control the molecular and

colloidal assembly as well as on the understanding of the underpinning physical phenomena.

The thesis deals with the different aspects of colloidal interactions and assembly of novel colloidal structures in thin nematic layers using optical tweezers. In particular, it is focused on: the measurement of interparticle forces, the (meta)stability of colloidal structures in uniform and chiral nematic fields, the assembly of 2D nematic colloidal crystals, the influence of induced disorder on stabilization of topological defects and finally, the complex entanglement of defect loops in a form of knots and links. The introductory part of the thesis (Chapter 4) presents achievements that have been obtained together with coworkers during the first two years of my research work, when I was focused on learning of experimental techniques and performing the detailed analysis of collected data. We have demonstrated for the first time that stable 2D nematic colloidal crystals can be built from elastic dipoles and quadrupoles in thin nematic layers using optical tweezers. The assembly process was studied also under applied electric field, which enabled the massive transport and crystallization of colloidal particles. Furthermore, we have discovered the unique binding mechanism, where colloidal particles are entangled by delocalized defect loops. That concept was applied to build entangled colloidal wires and hierarchical superstructures in mixtures of large and small particles. These results are quite to large extent presented in the following publications: *Science* [31], three *Physical Review E* [80–82], *Physical Review Letters* [83] and *European Physical Journal E* [96].

The main part of the thesis presents an expansion of our previous work. It is based on my original contributions and organized in three Sections of Chapter 5. In Section 5.1 we present the first experimental analysis of structural morphologies around non-spherical inclusions in confined nematic layers and demonstrate highly directional interparticle forces using optical tweezers. The results were published recently in *Soft Matter* [35]. Further, in Section 5.2 we have demonstrated how the chiral ordering of the underlying anisotropic fluid influences the defect formation and colloidal interactions in the geometry of a twisted nematic cell. The induced chirality stabilizes escaped non-singular defect rings, which are binding spontaneously formed particle pairs. The director escape mechanism also leads to the assembly of novel 2D nematic colloidal crystals of pure or mixed chirality. The results were published in *Physical Review Letters* [97]. Moreover, we have affirmed that escaped defect structures are related to entangled defect configurations and have shown how they can be reversely transformed one to another. The entangled structures, where particles and induced defect loops are inseparably connected in novel topologically bound objects, introduce a new perspective on the stabilization of colloidal dispersions. They possess interesting properties, such as chirality, strong string-like interparticle potential and non-trivial topological conformations. The most exciting results are presented in Section 5.3, where the discovery of knots and links, made from entangled defect lines in properly organized 2D particle arrays, is demonstrated. They represent a real manifestation of knot theory in a concrete physical phenomenon and allow to study various topological problems in a simple experimental system.

The thesis is organized as follows. In Chapter 2, the basic principles of Landau-de Gennes theory, surface anchoring, topological theory of nematic defects and mathematical theory of knots are reviewed. Chapter 3 introduces materials and experimental techniques that have been used for optical manipulation and imaging of colloidal particles in a liquid crystal host. Two important mechanisms of directed assembly of 2D nematic colloidal crystals in terms of elastic dipoles and quadrupoles, as well as discovery of 1D entangled colloidal structures, are presented in Chapter 4. The main results of the thesis are presented in Chapter 5. Section 5.1 is devoted to experimental analysis of structural morphologies in the vicinity of rod-like inclusions. Energetic stabilization of escaped defect rings, which allow the assembly of novel 2D nematic colloidal crystals in the geometry of a twisted nematic cell, is described in Section 5.2. The most interesting results of the thesis are extensively interpreted in Section 5.3, where we show that 2D entangled defect configurations in chiral nematic field can be generalized to topological conformations of knots and links. The final concluding Chapter 6 summarizes the main results and findings presented in the thesis.

Theoretical background

In this Chapter, a brief review of theoretical approaches based on phenomenological mesoscale modeling of the nematic liquid crystal is presented. Particular emphasis is given to the nematic order parameter, Landau-de Gennes free energy model, influence of an external electric field and surface anchoring interactions, which are commonly used as central elements in modeling of nematic liquid crystal colloids. Further, topological theory of nematic defects and multipole expansion approach for calculating interparticle potentials are briefly discussed. In addition, this Chapter introduces the fundamental concepts from mathematical theory of knots, relevant to issues of interest in the following Chapters of the thesis. This include basic definitions of knots and links, use of traditional knot type classification, introduction of topological invariants, knot polynomials and connection between knot theory and statistical mechanics through signed planar graphs.

2.1 Nematic order parameter

An isotropic liquid possesses neither positional nor orientational order and has thereby the highest possible symmetry. The nematic phase, on the other hand, is orientationally ordered, while positional order is still absent. Consequently, an order parameter containing information on solely orientational ordering of molecules is sufficient to characterize nematics and distinguish them from isotropic liquids. The nematic liquid crystal consists of rod-like molecules whose orientations can be characterized by unit vector $\mathbf{u}$ along the molecular long axis. Even when the building units are polar, molecular flips-flops and head-to-head overlapping establish the centrosymmetric average arrangement in the nematic bulk. To characterize orientational order of these molecules one requires a vectorial or tensorial order parameter field. The vectorial order parameter, usually referred to as *director* $\mathbf{n}(\mathbf{r}, t)$, describes the average orientation of nematic molecules at a given position $\mathbf{r}$ at time t , with orientations $\mathbf{n}(\mathbf{r}, t) \rightarrow -\mathbf{n}(\mathbf{r}, t)$ being equivalent. More precisely, the director $\mathbf{n}$ is defined as the ensemble average of molecular orientations $\mathbf{u}$ within a given volume or, due to ergodicity, as time average of a single molecule orientation at a given position. Anyway, it must be recalled that nematic phase is fluid, thus the centers of mass of the molecules are not long-range correlated, as in the case of liquid.

Orientational fluctuations of molecules around the director can be quantified by introducing the *scalar order parameter* S . Formally, S is defined as an ensemble average of the second Legendre polynomials evaluated from the scalar product between molecular orientations $\mathbf{u}$ and director $\mathbf{n}$. To show this, let us introduce a reference frame with z axis chosen to coincide with the director $\mathbf{n}$ and single molecule orientation accordingly parameterized with the polar and azimuthal angles, θ and ϕ , respectively, as $\mathbf{u} = (\cos \theta \sin \phi, \sin \theta \sin \phi, \cos \phi)$. The state of molecular alignment can be described by a distribution function $f(\theta, \phi)$, which gives the probability dP to find a molecule oriented within a solid angle $d\Omega$ as $dP = \frac{1}{4\pi} f(\theta, \phi) d\Omega$. In an undistorted sample $f(\theta, \phi)$ is *uniaxial*, axially symmetric with respect to $\mathbf{n}$, and hence ϕ independent. In such uniaxial nematics $f(\theta, \phi) = f(\theta)$ can be expanded as

$$f(\theta) = \sum_{n=0}^{\infty} f_n P_n(\cos \theta), \quad (2.1)$$

where $P_n(x)$ is the n th Legendre polynomial and $f_n = \frac{2n+1}{2} \int_{-1}^1 f(\theta) P_n(\cos \theta) d(\cos \theta)$. The monopole term is constant $f_0 = 1$ and odd terms ($n = 1, 3, \dots$) vanish due to the $\mathbf{u} \rightarrow -\mathbf{u}$ symmetry; hence $f(\theta) = f(\pi - \theta)$. The first non-zero contribution thus comes from the quadrupolar term f_2 , which is applied to define the scalar degree of order S :

$$S = \frac{1}{5} f_2 = \frac{1}{2} \int_{-1}^1 f(\theta) P_2(\cos \theta) d(\cos \theta) = \langle P_2(\cos \theta) \rangle, \quad (2.2)$$

where $\langle \dots \rangle$ denotes the average over an ensemble of molecules. The values of S lie in the interval $[-\frac{1}{2}, 1]$; $S = 1$ corresponds to a perfect nematic order with all molecules pointing exactly along the director, $S = 0$ characterizes a completely disordered (isotropic) state when the distribution of molecules is uniform over all directions, and $S = -\frac{1}{2}$ determines perfect molecular ordering within the plane perpendicular to $\mathbf{n}$. In typical nematics at room temperature S lies between 0.5 and 0.6 [98].

The director and the scalar order parameter can be further joined in a single tensorial order parameter. Rewriting the orientational probability function in terms of S up to the second order one obtains:

$$\begin{aligned} f(\theta) &= 1 + 5SP_2(\cos \theta) = 1 + \frac{5}{2}S(3(\mathbf{n} \cdot \mathbf{u})^2 - 1) = 1 + \frac{5}{2}S(3n_i n_j - \delta_{ij})u_i u_j \\ &= 1 + \frac{5}{2}S(3(\mathbf{n} \otimes \mathbf{n})_{ij} - I_{ij})u_i u_j = 1 + 5Q_{ij}^U u_i u_j, \end{aligned} \quad (2.3)$$

where summation over the repeated indices i, j is assumed, δ_{ij} is the Kronecker delta, I_{ij} is the identity matrix and $\mathbb{Q}^U$ is the *uniaxial tensorial order parameter*, introduced by:

$$\mathbb{Q}^U = \frac{1}{2}S(3\mathbf{n} \otimes \mathbf{n} - \mathbb{I}). \quad (2.4)$$

By definition, the tensor $\mathbb{Q}^U$ is symmetric and traceless. Its largest eigenvalue is nematic degree of order S and the corresponding eigenvector is director $\mathbf{n}$. The other two eigenvalues are equal to $-\frac{1}{2}S$ and eigenvectors are perpendicular to $\mathbf{n}$.

Under external constraints, such as electric and magnetic fields or severe confinement, elastic deformations can break the cylindrical symmetry of the $f(\theta, \phi)$ distribution function, assumed so far. In addition to the director $\mathbf{n}$, two additional directions appear in the system, $\mathbf{e}_1$ and $\mathbf{e}_2$, forming an orthonormal triad together with $\mathbf{n}$. In such biaxial nematics the tensorial order parameter can be expanded into the *full order parameter tensor* $\mathbb{Q}$ as:

$$\mathbb{Q} = \frac{1}{2}S(3\mathbf{n} \otimes \mathbf{n} - \mathbb{I}) + \frac{1}{2}\mathcal{B}(\mathbf{e}_1 \otimes \mathbf{e}_1 - \mathbf{e}_2 \otimes \mathbf{e}_2), \quad (2.5)$$

introducing $\mathcal{B} = \frac{3}{2}\langle \sin^2 \theta \cos 2\phi \rangle$ as the *biaxiality*. The values of $\mathcal{B}$ lie in the interval $[-\frac{3}{2}, \frac{3}{2}]$, where $\mathcal{B} = 0$ characterizes uniaxial ordering and $|\mathcal{B}| = \frac{3}{2}$ corresponds to the perfect biaxial ordering. Order parameter tensor $\mathbb{Q}$ is like $\mathbb{Q}^U$ symmetric and traceless. It has five degrees of freedom that can be easily recognized: orientation of the director (two angles), orientation of the secondary director relative to the director (one angle), scalar order parameter S and biaxiality $\mathcal{B}$. By diagonalizing $\mathbb{Q}$ three different eigenvalues are obtained: S , $-\frac{1}{2}(S + \mathcal{B})$ and $-\frac{1}{2}(S - \mathcal{B})$ with the corresponding eigenvectors equalling $\mathbf{n}$, $\mathbf{e}_1$ and $\mathbf{e}_2$, respectively.

2.2 Landau-de Gennes theory

2.2.1 Nematic-isotropic phase transition

In phase transitions matter undergoes changes in microstructure and symmetry. Usually, a phase transition is accompanied by the change of a macroscopic observable like density, electric, magnetic and optical properties. While the relevant thermodynamic potential, determining the equilibrium state in a system for given parameters (free energy F for well-defined temperature, volume and particle number), remains continuous across the transition, its derivatives may not. Phase transitions characterized by a discontinuity in entropy $\mathcal{S} = -(\partial F/\partial T)_V$ are referred as *discontinuous* or first order, while the ones with no discontinuity in $\mathcal{S}$ are called *continuous* or second order. The possible discontinuity in entropy, $\Delta\mathcal{S}$, results in an exchange of latent heat $\mathcal{Q} = T_c\Delta\mathcal{S}$, where T_c stands for the transition temperature. Moreover, metastable states can be found in the vicinity of discontinuous transitions.

In this work we are interested in thermotropic liquid crystals, where the temperature determines whether the molecules are in the isotropic, nematic or glassy mesophase. The temperature is also the main parameter that drives transitions between different mesophases. Experimental studies have shown that the nematic-isotropic (N-I) phase transition is accompanied both by a discontinuous drop in order parameter S and by absorption of the latent heat [8]. The latent heat for a typical 5CB nematic liquid crystal is 1560 J/kg [99], which is roughly 0.5 % of the latent heat in the ice-water phase transition. The N-I transition temperature T_{NI} for the 5CB material is 308.4 K, but can vary substantially for different materials.

An established approach to describe the N-I phase transition is to use the invariants of the nematic order parameter tensor and construct a free energy functional as a Landau expansion. The minimal free energy volume density f_{ORD} needed to model the N-I transition reads [8]:

$$f_{ORD} = \frac{1}{2}a(T - T_{NI}^*)\text{tr}\mathbb{Q}^2 + \frac{1}{3}B\text{tr}\mathbb{Q}^3 + \frac{1}{4}C(\text{tr}\mathbb{Q}^2)^2, \quad (2.6)$$

where $a > 0$, $B < 0$ and $C > 0$ are phenomenological material constants, while T_{NI}^* is the super-cooling temperature. Typically, a is of order of 10^5 J/m³K, while $B \sim -10^6$ J/m³ and $C \sim 10^6$ J/m³. In the nematic phase both first and second prefactor in the expansion are negative and only $C > 0$ ensures that the free energy density functional is bounded from below and agrees with the symmetry of the order parameter S . Unlike constants B and C , the first prefactor $a(T - T_{NI}^*)$ is temperature dependent and therefore drives the N-I transition.

Free energy functional which drives the N-I transition in terms of the nematic degree of order can be projected from Eq. (2.6) by assuming uniaxial ordering of the nematic, $\mathbb{Q}^U = \frac{1}{2}S(3\mathbf{n}\otimes\mathbf{n}-\mathbb{I})$. Trace invariants of the uniaxial order parameter tensor simplify as $\text{tr}(\mathbb{Q}^U)^2 = \frac{3}{2}S^2$ and $\text{tr}(\mathbb{Q}^U)^3 = \frac{3}{4}S^3$. Rewriting f_{ORD} in terms of S one gets:

$$f_{ORD} = \frac{3}{4}a(T - T_{NI}^*)S^2 + \frac{1}{4}BS^3 + \frac{9}{16}CS^4. \quad (2.7)$$

Now f_{ORD} is dependent only on S and the role of all three Landau expansion terms become clear to interpret: first term drives the transition, second term is allowed by symmetry $S \neq -S$, while the third term bounds the value of S from below. The equilibrium in the system is then found by minimizing the free energy $F_{ORD} = \int f_{ORD}dV$ at fixed temperature with respect to S_{eq} , yielding:

$$S_{eq} = \begin{cases} 0, & T > T_{NI}, \\ \frac{B}{2C} \left(1 + \sqrt{1 - \frac{4aC}{B^2}(T - T_{NI}^*)} \right), & T < T_{NI}. \end{cases}$$

Analyzing the stability of the solutions given in the above expression leads to the following relations: the phase transition temperature T_{NI} is related to the super-cooling temperature T_{NI}^* via $T_{NI} = T_{NI}^* + 2B^2/9aC$, while the highest temperature of the super-heated nematic phase

T_{NI}^{**} is given by $T_{NI}^{**} = T_{NI}^* + B^2/4aC$. The physical interpretation of the temperatures T_{NI}^* , T_{NI} and T_{NI}^{**} is clear from free energy density profiles at various temperatures, presented in Fig. 2.1.

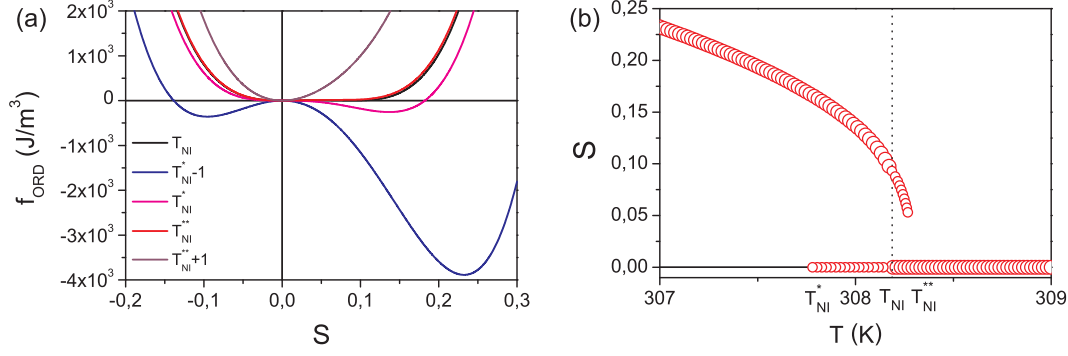


Figure 2.1: (a) Free energy density f_{ORD} as a function of the order parameter for several temperatures T , both below and above T_{NI} . Note the changes in the free energy minima for different T . (b) Degree of nematic order S as a function of temperature T . A discontinuous jump in the order parameter and super-cooling/super-heating regions are the imprints of the first order phase transition.

2.2.2 Nematic elasticity

In confined nematic system the solid substrate imposes a degree of order typically different from the equilibrium bulk value S_{eq} and, as a consequence, the orientational ordering becomes spatially-dependent. However, any elastic deformation of the nematic fluid can be decomposed in three distinct deformation modes, known as *splay*, *twist* and *bend*, and presented in Fig. 2.2.

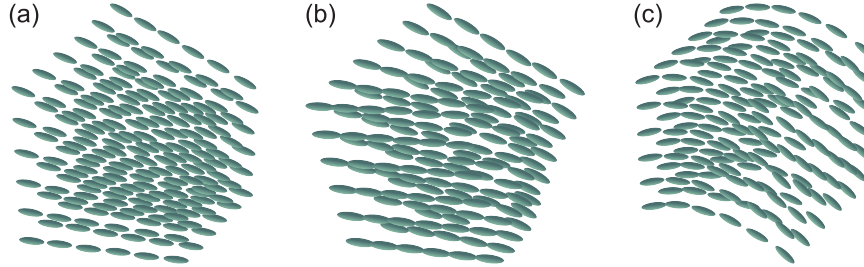


Figure 2.2: Elastic deformation modes: (a) splay, (b) twist, and (c) bend.

In the weak deformation limit the first order space derivatives $\partial Q_{ij}/\partial x_k$ of the $\mathbb{Q}$ tensor are small quantities and therefore can be used to construct additional scalar invariants with the proper symmetry, representing free energy contributions associated with elastic distortions. The common formulation of the elastic free energy volume density f_E reads [8,100]:

$$f_E = \frac{1}{2}L_1 \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k} + \frac{1}{2}L_2 \frac{\partial Q_{ij}}{\partial x_j} \frac{\partial Q_{ik}}{\partial x_k} + \frac{1}{2}L_3 Q_{ij} \frac{\partial Q_{kl}}{\partial x_i} \frac{\partial Q_{kl}}{\partial x_j}, \quad (2.8)$$

where L_1 , L_2 , and L_3 are elastic constants, x_i are Cartesian coordinates and summation over repeated indices is assumed. Three elastic constants are introduced in order to account for the three basic deformation modes. The L_i are independent of the nematic degree of order and should be interpreted as the direct strength of the intermolecular interactions.

Elastic free energy f_E based on the order parameter tensor can be rewritten for a uniaxial nematic in terms of the director $\mathbf{n}$ [101]. Using $\mathbb{Q}^U = \frac{1}{2}S(3\mathbf{n} \otimes \mathbf{n} - \mathbb{I})$, $S = \text{const.}$, $\mathbf{n} \cdot \mathbf{n} = 1$ and hence $n_i(\partial n_i/\partial x_k) = 0$, the elastic free energy density in the Frank-Oseen form reads as:

$$f_E^{FO} = \frac{1}{2}K_{11}(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_{22}[\mathbf{n} \cdot (\nabla \times \mathbf{n}) + q_0]^2 + \frac{1}{2}K_{33}[\mathbf{n} \times (\nabla \times \mathbf{n})]^2, \quad (2.9)$$

where K_{ii} are Frank elastic constants given as combinations of L_i [100]: $L_1 = (K_{33} + 2K_{22} - K_{11})/(9S^2)$, $L_2 = 4(K_{11} - K_{22})/(9S^2)$ and $L_3 = 2(K_{33} - K_{11})/(9S^3)$. The constants K_{ii} are proportional to S^2 and incorporate the degree of nematic order as an internal parameter. The advantage of using the K_{ii} set of constants is that they directly characterize basic deformation modes: K_{11} splay with $(\nabla \cdot \mathbf{n})^2 \neq 0$, K_{22} twist with $[\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 \neq 0$ and K_{33} bend with $[\mathbf{n} \times (\nabla \times \mathbf{n})]^2 \neq 0$. The constant q_0 , appearing in the twist invariant is permitted on symmetry grounds only in systems lacking inversion symmetry, namely chiral liquid crystals. In such chiral systems this coefficient serves to promote a naturally distorted texture in which director displays a pure twist distortion with $\mathbf{n} \cdot (\nabla \times \mathbf{n}) = -q_0$. It may readily be verified that the director field $\mathbf{n} = (0, \cos(q_0 x), \sin(q_0 x))$ satisfies this relation. It describes a helical texture known as the cholesteric phase in which the director rotates moving along the helical axis, but is uniform perpendicular to it. The director undergoes a complete revolution over a distance of $\frac{2\pi}{q_0}$, but because of its apolar character the physical repeat length, known as pitch, is precisely half of this value, equalling $p = \frac{\pi}{q_0}$.

The Frank-Oseen free energy can be further extended by the divergence energy density terms f_{13} [102] and f_{24} [103], allowed by the symmetry:

$$f_{13} = K_{13} \nabla \cdot [\mathbf{n}(\nabla \cdot \mathbf{n})], \quad (2.10)$$

$$f_{24} = -K_{24} \nabla \cdot [\mathbf{n}(\nabla \cdot \mathbf{n}) + \mathbf{n} \times (\nabla \times \mathbf{n})], \quad (2.11)$$

where K_{13} and K_{24} are mixed *splay-bend* and *saddle-splay* elastic constants, respectively. The effect of K_{13} and K_{24} contributions is, however, limited to the surface of the liquid crystals. The saddle-splay K_{24} term gives spatial derivatives of the director within the surface plane, whereas mixed splay-bend term allows derivatives within the surface plane and along the plane normal [104]. Contributions of both K_{24} and K_{13} roughly affect the bulk behavior of the liquid crystal only through the renormalization of surface anchoring. Nevertheless, divergence volume density terms can be directly transformed into surface density using Gauss theorem.

Elastic free energy volume densities, described by Eqs. (2.8) and (2.9), are complex spatially dependent functionals when used with all three elastic constants. A common approach to simplify these functionals is to use *one elastic constant approximation*, which sets $L_1 = L$, $L_2 = L_3 = 0$ and $K_{11} = K_{22} = K_{33} = K$. The free energies f_E and f_E^{FO} within the one elastic constant approximation are then written as:

$$f_E = \frac{1}{2} L \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k}, \quad (2.12)$$

$$f_E^{FO} = \frac{1}{2} K [(\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2]. \quad (2.13)$$

The suitability of the one elastic constant approximation depends strongly on the material. The typical magnitude of Frank elastic constants for 5CB nematic is $K \sim 6 \cdot 10^{-12}$ N, but they can differ from the average value up to 40 % [105].

2.2.3 Landau-de Gennes free energy

Elastic free energy f_E and free energy characterizing nematic degree of order f_{ORD} constitute Landau-de Gennes (LdG) free energy model when combined into a single functional. Denoting the total LdG free energy volume density as f_{LdG} , one can write:

$$f_{LdG} = f_E + f_{ORD}. \quad (2.14)$$

Landau-de Gennes model is the central phenomenological model for nematic liquid crystals at (sub)micrometer scale as it incorporates both nematic elasticity and spatial variation of the nematic degree of order. It can be applied for arbitrary geometry, different length scales and

is easily extendable to include the effects of external fields. The only limitation of LdG model is that it becomes less reliable at nanometer scale because of its mean-field character. Order parameter tensor, used as the main element of the model, namely assumes an ensemble average of molecular orientations, which have typically few nanometers in length.

The ratio of the two energy contributions in LdG free energy introduces a characteristic length of the S variation, referred to as *nematic correlation length* ξ_N . To extract ξ_N from f_{LdG} , we rewrite the free energy density f_{LdG} within the one elastic constant approximation using uniaxial order parameter tensor $\mathbb{Q}^U$ and assuming spatial variations of S alone ($\nabla S \neq 0, \nabla \mathbf{n} = 0$):

$$f_{LdG} = \frac{3}{4}a(T - T_{NI}^*)S^2 + \frac{1}{4}BS^3 + \frac{9}{16}CS^4 + \frac{3}{4}L(\nabla S)^2. \quad (2.15)$$

In order to find the equilibrium S profile, the f_{LdG} has to be minimized with the Euler-Lagrange formalism:

$$\frac{3}{2}L\nabla^2 S - \frac{\partial f_{LdG}}{\partial S} = 0. \quad (2.16)$$

By linearizing the Euler-Lagrange equation for small spatial perturbations from the equilibrium, $S(x_i) = S_{eq} + \Delta S(x_i)$, where $\Delta S(x_i) \propto \exp(\frac{x_i}{\xi_N})$, the nematic correlation length is obtained:

$$\xi_N = \sqrt{\frac{3}{2} \frac{L}{\frac{\partial^2 f_{LdG}}{\partial S^2}|_{S_{eq}}}} = \sqrt{\frac{L}{a(T - T_{NI}^*) + BS_{eq} + \frac{9}{2}CS_{eq}}}. \quad (2.17)$$

The correlation length ξ_N increases on approaching the transition temperature T_{NI} from either side, but does not diverge. $S_{eq} = 0$ in the isotropic phase ($T > T_{NI}$) and $S_{eq} \neq 0$ in the nematic phase ($T < T_{NI}$). Its role in typical nematic is most pronounced in defect cores, as it roughly determines their size. Typically, ξ_N is at the order of few nanometers and similar characteristic length can be derived for biaxiality variations as well.

2.3 Surface anchoring

Interfaces with solid, liquid or gas materials affect liquid crystal ordering by imposing a preferred degree of order and a preferred average molecular orientation, the *easy axis*, alternatively denoted by the surface-preferred order parameter tensor $\mathbb{Q}_0$. Such behavior is usually referred to as *anchoring* [22] and it was first discovered in 1913 by Charles Mauguin [106], who found that a nematic liquid crystal is aligned with its axis parallel to the surface, making an angle of 60° with the optical axis of the mica slide. The most common types of anchoring are planar and perpendicular (homeotropic) ordering with respect to the surface (see Fig. 2.3). Any deviations from the interface-imposed ordering are penalized by a surface contribution to free energy, which can be written in terms of appropriate scalar invariants. These are now constructed from the tensor $\mathbb{Q}_s - \mathbb{Q}_0$, measuring the deviation of the actual surface ordering $\mathbb{Q}_s$ from $\mathbb{Q}_0$. The corresponding bulk free energy density reads:

$$f_a(\mathbf{r}) = \frac{1}{2}W_e \left[\text{tr}(\mathbb{Q}_s - \mathbb{Q}_0)^2 + \mu(\text{tr}(\mathbb{Q}_s - \mathbb{Q}_0)^2)^2 \right] \delta(\mathbf{r} - \mathbf{r}_0). \quad (2.18)$$

Mostly, it is enough to consider the first contribution only, setting $\mu = 0$ [107]. Since the van der Waals forces, mainly responsible for anchoring effects, are relatively short ranged, f_a is regarded as a purely contact term and $\mathbf{r}_0$ is representing the locus of points defining the interface. The quantity W_e has units of energy and is related to the strength of the anchoring. For uniaxial nematics with $\mathbb{Q}_0 = \frac{1}{2}S_0(3\mathbf{n}_0 \otimes \mathbf{n}_0 - \mathbb{I})$ and $\mathbb{Q}_s = \frac{1}{2}S_s(3\mathbf{n}_s \otimes \mathbf{n}_s - \mathbb{I})$ the lowest order term in expression (2.18) reduces to a surface free energy density:

$$f_s = \frac{9}{8}W_e \left[\frac{2}{3}S_s^2 + \frac{2}{3}S_0^2 - 2S_sS_0 \left((\mathbf{n}_s \cdot \mathbf{n}_0)^2 - \frac{1}{3} \right) \right]. \quad (2.19)$$

Now $\mathbf{n}_0$ and S_0 stand for the direction of the easy axis and for the surface-induced value of S , respectively, while $\mathbf{n}_s$ and S_s represent their actual surface values. In cases without S variation ($S_0 = S_s = S_b$), the above expression simplifies to:

$$f_s^{uni} = -\frac{1}{2}W_e^{uni} \cos^2 \alpha, \quad (2.20)$$

retaining the term with angular dependence only. This Rapini-Papoular form [108] of surface free energy density functional often represents a good enough approximation for the anchoring energy. Here $\cos \alpha = \mathbf{n}_s \cdot \mathbf{n}_0$ has been introduced and α represents the angular deviation of the surface director $\mathbf{n}_s$ from the easy axis $\mathbf{n}_0$. Furthermore, the uniform surface anchoring strength has been introduced as $W_e^{uni} = \frac{9}{2}W_e S_b^2$. Typically, values of W_e^{uni} range from 10^{-3} J/m² to 10^{-7} J/m² [109], where 10^{-3} J/m² is considered strong anchoring and 10^{-7} J/m² weak anchoring.

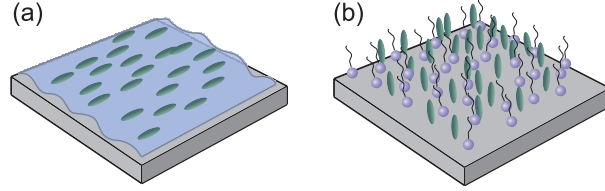


Figure 2.3: (a) Liquid crystal molecules can be well-aligned using the treatments of a surface with rubbed polyimide resulting in planar anchoring. (b) Homeotropic alignment can be achieved by coating a substrate with a surfactant containing aliphatic tails, where the polar head groups bind to the substrate, creating a forest of aliphatic tails and making liquid crystal molecules to stand up amongst these tails.

The strength of the uniform surface anchoring can be interpreted also in terms of Kleman-de Gennes *surface extrapolation length* ξ_S [8,110]. The latter is defined as $\xi_S = K/W_e^{uni}$, where K is the effective Frank elastic constant and measures relative strength of nematic elasticity with respect to the surface anchoring. Formally, we introduce it in a nematic slab with two surfaces of dissimilar anchoring imposing bend-splay nematic deformation [111]. The first surface imposes infinitely strong uniform planar anchoring as anchoring in the second surface is homeotropic and finite. In a thick enough sample such a geometry induces an elastic deformation, where the relative angle ϕ of the director with respect to the surface normal z is linear along z (see Fig. 2.4). The extrapolation scale of this local director variation, caused by the finite surface anchoring, is the surface extrapolation length. Note that for strong enough anchoring it is possible to determine ξ_S simply by extrapolating the $\phi(z)$ profile graphically across the sample boundary to $\phi = 0$, corresponding to the homeotropic easy axis [111]. Note also that if the degree of nematic order is allowed to vary, which is usually the case near confining boundaries, the profile $\phi(z)$ may deviate from the linear behavior predicted above. For a typical nematic ($K \sim 10^{-11}$ N), confined between the surfaces with strong anchoring ($W_e^{uni} \sim 10^{-3}$ J/m²), one gets extrapolation length in the order of 10 nm, while for surfaces with weak anchoring ($W_e^{uni} \sim 10^{-6}$ J/m²) ξ_S corresponds approximately to 10 μ m.

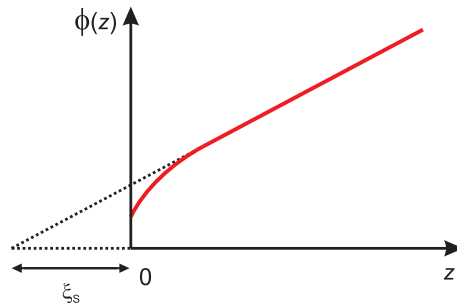


Figure 2.4: Surface extrapolation length ξ_S as introduced in the bend-splay nematic cell [8].

2.4 Influence of an external electric field

There are four basic mechanisms of interactions between the applied electric field and the liquid crystal: (i) dielectric, (ii) flexoelectric, (iii) through surface polarization originating from electric double layers of ions, and (iv) through the motion of electric carriers. To simplify things, we temporarily neglect the flexoelectric effect and assume that the liquid crystal is a perfect insulator and that there is no surface polarization at the boundaries.

When nematic molecules are exposed to an external field, an additional contributions appear in the bulk free energy density. External electric field couples with the non-polar nematic medium through a dielectric interaction with the induced dipoles of nematic molecules. These dipoles are oriented either parallel or perpendicular to the director, depending on the polarizability of nematic molecules with either positive or negative dielectric anisotropy ϵ_a . Within the framework of Landau-de Gennes theory, the dielectric coupling is introduced as an additional free energy density contribution f_e [100]:

$$f_e = -\frac{1}{2}\epsilon_0\left(\bar{\epsilon}E_i^2 + \frac{2}{3}\epsilon_a^{mol}Q_{ij}E_iE_j\right), \quad (2.21)$$

where ϵ_0 is the dielectric vacuum permittivity, $\bar{\epsilon} = \frac{1}{3}(2\epsilon_{\perp} + \epsilon_{\parallel})$ is the average liquid crystal permittivity, $\epsilon_a^{mol} = \epsilon_{\parallel}^{mol} - \epsilon_{\perp}^{mol}$ is the molecular dielectric anisotropy (macroscopic dielectric anisotropy reads $\epsilon_a = S\epsilon_a^{mol}$) and E_i is the external electric field. Eigenvalues of the molecular dielectric permittivity tensor $\epsilon_{\perp}^{mol}$ and $\epsilon_{\parallel}^{mol}$ correspond to eigenvectors perpendicular and parallel to the director, respectively. Typical values for 5CB at room temperature are $\epsilon_a \approx 11$ and $S = 0.525$, providing $\epsilon_a^{mol} \approx 21$ [112].

The relative effect of the electric field to nematic dielectric coupling is characterized by the *electric coherence length*. It is introduced as $\xi_E = \sqrt{K/\epsilon_0\epsilon_a E^2}$ [8] and it gives the relative ratio between reorientation effects caused by nematic elasticity and reorientation caused by the electric field. Formally, it can be recognized as the intrinsic scale of the Euler-Lagrange equation governing the reorientation of the nematic, caused by the external field. Using director $\mathbf{n} = (\sin \phi, 0, \cos \phi)$, where $\phi = \phi(z)$ is the angle between the director and the surface normal, single constant elastic free energy $\frac{1}{2}K(\frac{\partial \phi}{\partial z})^2$, dielectric free energy $-\frac{1}{2}\epsilon_0\epsilon_a(\mathbf{n} \cdot \mathbf{E})^2$ and assuming uniform electric field $\mathbf{E} = (0, 0, E)$, the Euler-Lagrange equation reads $K\frac{\partial^2 \phi}{\partial z^2} - \epsilon_0\epsilon_a E^2 \sin 2\phi$. Finally, by transforming it into dimensionless form, ξ_E is obtained [8]. To generalize, dielectric coupling between nematic and electric field is important at scales smaller than ξ_E but can be omitted at scales larger than ξ_E . For a typical nematic ($K \sim 10^{-11}$ N, $\epsilon_a \approx 10$) and electric field $E = 1$ V/ μm , the electric coherence length ξ_E corresponds to 0.3 μm .

In a planar cell, where the nematic is sandwiched between two parallel oriented substrates, however, in a weak field applied along the cell normal, the nematic remains undeformed. The deformation appears only above a certain threshold value that is inversely proportional to the sample thickness h , which is phenomenon known as the *Fréedericksz transition* [113,114]. It is a continuous structural transition, threshold of which can be estimated by studying the stability of the $\phi(z) = \frac{\pi}{2}$ zero field solution with respect to small perturbations. Decomposing these into Fourier components, the component with the largest possible wavelength is found to be destabilized first. Expressed in terms of the electric coherence length, for strong anchoring the Fréedericksz transition occurs at $\xi_E^F = \frac{h}{\pi}$ [8]. For finite anchoring, however, the threshold shifts towards lower field strengths. For $\xi_S \ll h$, ξ_E^F is modified to $\xi_E^F = \frac{h}{\pi}(1 + 2\xi_S h)$ [109] and at high enough field strengths, the field-aligned structure takes place.

As already indicated, the effects of the electric field are complicated by mechanisms different from the dielectric coupling (flexoelectricity, surface polarization and free ions). Flexoelectricity in liquid crystals is an analog of piezoelectricity in solid crystals [115]. Splay and bend deformation of the nematic director can induce macroscopic flexoelectric polarization of the medium [104]. The effect can be qualitatively illustrated by observing the orientational ordering

of anisometric molecules that have permanent electric dipole moments. Figure 2.5 shows how pear-shaped and banana-shaped molecules create a net non-zero macroscopic polarization when subjected to splay and bend elastic deformation, respectively. Macroscopic polarization in the nematic liquid crystal can be induced also by the gradients of the nematic degree of order S , which is known as *order electricity* [116,117]. In particular, order electricity is important at the nematic-isotropic interfaces as it affects the preferential orientation of the nematic molecules.

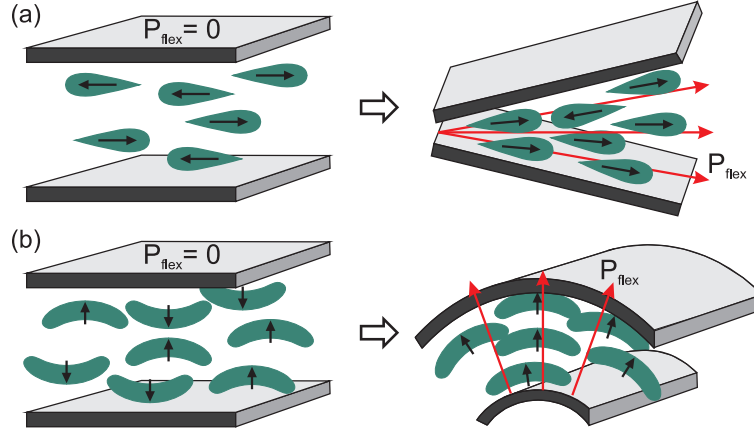


Figure 2.5: (a) Pear-shaped molecules effectively generate macroscopic flexoelectric polarization $\mathbf{P}_{flex}$ when subjected to splay elastic deformation, whereas (b) banana-shaped molecules generate $\mathbf{P}_{flex}$ when subjected to bend. Adapted from Ref. [104].

In order to account for both flexoelectricity and order electricity, the total macroscopic polarization induced by the deformation of the liquid crystal $\mathbf{P}^{tot}$ is introduced by using the nematic order parameter tensor:

$$P_i^{tot} = G_{ijkl} \frac{\partial Q_{jk}}{\partial x_l}. \quad (2.22)$$

Here, G_{ijkl} are the components of the fourth rank coupling tensor, which incorporates flexoelectric coefficients e_1 and e_3 and order electricity coefficients r_1 and r_2 [117]. For 5CB, coefficients e_i are of the order of 10^{-11} As/m [118]. The standard flexoelectric polarization in terms of the director $\mathbf{P}_{flex} = e_1 \mathbf{n}(\nabla \cdot \mathbf{n}) + e_3 (\nabla \times \mathbf{n}) \times \mathbf{n}$ and the order electricity polarization in terms of the nematic degree of order $\mathbf{P}_{ord} = r_1 \mathbf{n}(\mathbf{n} \cdot \nabla)S + r_2 \nabla S$ are obtained if imposing symmetry constraints on G_{ijkl} and assuming uniaxiality of the order parameter tensor, $Q^U = \frac{1}{2}S(3\mathbf{n} \otimes \mathbf{n} - \mathbb{I})$.

The macroscopic polarization couples to the electric field. The corresponding free energy volume density f_{flex} reads:

$$f_{flex} = -\mathbf{P}^{tot} \cdot \mathbf{E}, \quad (2.23)$$

where $\mathbf{E}$ is the total electric field. Typically, $\mathbf{E}$ is the external field, however, in general contributions to the field generated by the polarization $\mathbf{P}^{tot}$ also have to be included. Effects of the flexoelectricity and order electricity are typically small in the absence of the external fields (at the order of less than 1 % in the total free energy), but can affect local structure of particular defects, where deformation of the nematic is strong. Another linear electric effect occurs when the heads and tails of molecules have different affinity with the bounding surface. If these molecules have longitudinal dipole moments, the broken surface symmetry results in a surface polarization $\mathbf{P}_{surf}$ and a contribution $-\mathbf{P}_{surf} \cdot \mathbf{E}$ to the free energy density [104]. Surface polarization typically results from the electric double layers formed by selective ion adsorption at interfaces [18,119]. Ions are always present in liquid crystals, either as the residuals of the chemical synthesis or because of the injection from the electrodes under applied voltage. Therefore variety of electro-hydrodynamic effects occur when the current of ions drags the liquid crystal in motion.

2.5 Topological theory of nematic defects

Topological defects [120–122], the necessary consequence of broken symmetry, exist in systems as disparate as superfluid helium ^3He [123], crystalline solids, liquid crystals [124] and quantum Hall fluids [125]. They play an important, if not determining role in such phenomena as response to external stresses, the nature of phase transitions [126] or the approach to equilibrium after a quench into an ordered phase [127], and they even arise in certain cosmological models [128]. Given the universal nature of topological defects, it is always interesting to find new systems that allow us to complement our knowledge of these phenomena.

Liquid crystals are ideal materials for studying topological defects. In a real macroscopic sample one almost never encounters the perfect homogeneous director pattern, but typically finds a distribution of diversely oriented nematic domains instead. Wherever these domains meet, topological defects emerge. Distortions yielding defects are easily produced through control of boundary conditions, surface geometry and external fields [129]. At molecular level the resulting defects are characterized by strong alternations of the molecular orientations, accompanied by a significant decrease in the degree of nematic ordering S to avoid the high deformation free energy cost, and by non-negligible biaxiality $\mathcal{B}$. On the macroscopic level supra-micrometer-sized topological defects are easily imaged optically due to the large birefringence of liquid crystalline material, thus providing us detailed and visually striking information about their emergence and dynamics.

There are two types of topological defects in the uniaxial nematic phase: line defects, called *disclinations*, and point defect, called *hedgehogs* [104,129]. Using topology to characterize defects, one can attribute to a line defect a topological invariant called *winding number*, whereas to each point defect a *topological charge* can be assigned [121,129]. Lines in form of loops are topologically equivalent to points. Typical director configurations for two line defects with the winding numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ are shown in Fig. 2.6(a, b). Point defects with the topological charges $+1$ and -1 are schematically presented in Fig. 2.6(c, d).

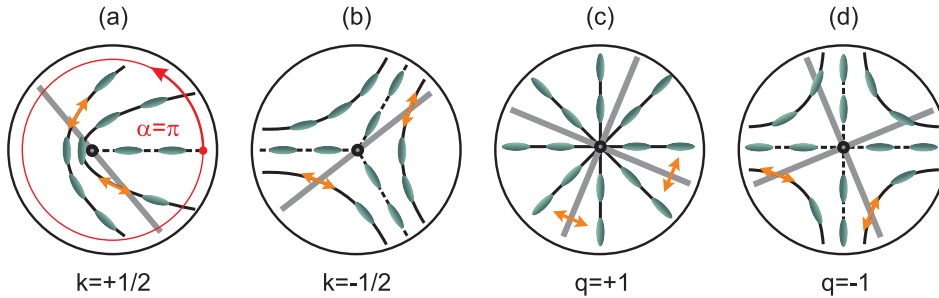


Figure 2.6: Director field configurations surrounding topological defects of different strength. (a,b) Liquid crystal defect lines with the winding numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ are presented with black lines indicating the geometrical arrangement of the molecules. (c,d) Point defects with the topological charges $+1$ and -1 . The gray lines represent the regions of light extinction between crossed polarizers and correspond to dark fringes when observed under depolarized light [8]. The directions of polarizers are shown by orange arrows, while the direction of molecular revolution is assigned by the red arrow.

Winding number (strength) of a disclination line k characterizes the local symmetry of the surrounding director field. It is introduced as a ratio $k = \frac{\alpha}{2\pi}$, where α represents the angle by which the director rotates along a closed loop surrounding the disclination line [104]. The geometrical representation of k is clearly seen if calculating the director field surrounding the defect line. Using one elastic constant approximation, elastic free energy f_E^{FO} [Eq. (2.13)] and the simplest disclination configuration, shown in Fig. 2.6(a), the director is $\mathbf{n} = (\cos \frac{\phi}{2}, \sin \frac{\phi}{2}, 0)$, where $\phi = \tan^{-1} \frac{y}{x}$ is the azimuthal angle in the (x, y) plane. Thus one gets, by minimization, the Euler-Lagrange equation $\nabla^2 \phi = 0$. The solution of the Laplacian in cylindrical coordinates

(r, θ, z) , when applying the hodograph rule $\oint d\phi = 2\pi k$ [130], reads as:

$$\phi = k\theta + c(r, \theta), \quad (2.24)$$

where $c(r, \theta)$ is a general function, harmonic and regular at the origin. The above choice for $c(r, \theta)$ merely defines the relative orientation of the director field with respect to the coordinate frame. Rewriting the director, the structure around the disclination line depends only on the winding number k :

$$\mathbf{n} = (\cos(k\theta + c), \sin(k\theta + c), 0). \quad (2.25)$$

By integrating f_E^{FO} over (r, θ) , one can calculate the energy per unit length W_{DL} of the disclination line from the director profile using the equation [124]:

$$W_{DL} = \pi K k^2 \ln \frac{R}{r_c} + W_c, \quad (2.26)$$

where R is the size of the system, r_c is the radius of the disclination core and W_c corresponds to the core energy per unit length [130,131]. The internal scale of the defects, core radius r_c and energy W_c are introduced in order to avoid the discontinuity of the director field in the center of the defects, when calculating W_{DL} . The proportionality $W_{DL} \propto k^2$ in Eq. (2.26) explains that in nematics $+\frac{1}{2}$ and $-\frac{1}{2}$ disclination lines are the only energetically favorable type of defects. Furthermore, the enormous energy cost of $k = \pm 1$ disclinations can be avoided by allowing the director to escape into the third dimension, becoming perpendicular to the page in Fig. 2.6, at the center of the defect [131–133]. Such situation was experimentally observed in liquid crystals confined to cylindrical capillaries [8,134,135], and more recently in nematic colloids [131,136]. This non-singular defect configuration, generated by a compromise between geometry and boundary conditions, will be the principal focus of Section 5.2.

Topologically, any director configuration can be mapped on a half sphere S^2/Z_2 with a unit radius [104]. Considering now the director along a closed loop surrounding a line defect in the director space, it can be mapped to a contour in the order parameter space. Two types of contours are possible, depending on the director configuration (see Fig. 2.7). A closed contour implies that the loop in the director field space surrounds a topologically unstable defect configuration, being either an integer line defect or an elastically distorted sample. Such configuration is topologically equivalent to a uniform nematic as the contour in the order parameter space can be shrunk continuously to a single point. A non-closed contour terminating at two diametrically opposite points characterizes a half-integer defect structure, which is topologically stable as it can not be contracted to a point. Both energetically and topologically stable $+\frac{1}{2}$ and $-\frac{1}{2}$ defect lines belong to the same class as they can be smoothly transformed one into another, as schematically shown in Fig. 2.7(b).

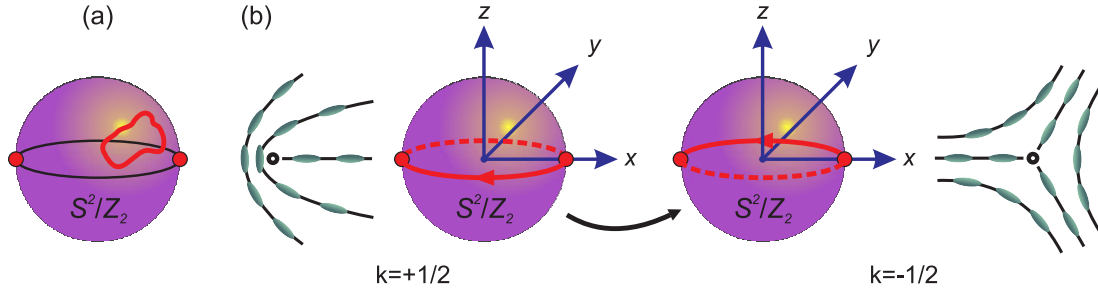


Figure 2.7: (a) Director order parameter space S^2/Z_2 : a closed contour in red corresponds to a topologically unstable defect configuration, a contour terminating at two diametrically opposite points characterizes a half integer defect line. (b) $+\frac{1}{2}$ disclination line can be smoothly transformed into a $-\frac{1}{2}$ line. Contours are smoothly transformable within the order parameter space. Adapted from Ref. [137].

Topological charge of a point defect q is introduced as an integral over a closed surface σ surrounding the defect core and reads as [129,130,138]:

$$q = \frac{1}{8\pi} \oint_{\sigma} \epsilon_{ijk} \mathbf{n} \cdot \left(\frac{\partial \mathbf{n}}{\partial x_j} \times \frac{\partial \mathbf{n}}{\partial x_k} \right) dS_i, \quad (2.27)$$

where ϵ_{ijk} is the Levi-Civita totally asymmetric tensor and x_i are Cartesian coordinates. Equation (2.27) is odd in $\mathbf{n}$, so that a selected hedgehog can have positive or negative charge due to nematic inversion symmetry $\mathbf{n} \rightarrow -\mathbf{n}$. Nevertheless, one conventionally assigns the value $+1$ to a radial hedgehog and -1 to a hyperbolic hedgehog. Note that the surface σ , which surrounds the considered defects, should be defect-free.

Topologically, charge can be considered as mapping Σ of the director profile from the closed surface σ to the order parameter space of the unit sphere S^2 . If Σ covers S^2 only partially, the defect configuration within σ is topologically unstable and is equivalent to the uniform field. Such mapping can be contracted to a single point [see Fig. 2.8(a)]. Mappings Σ , which cover the full order parameter unit sphere, however, can not be contracted and thus characterize topologically stable point defects [see Fig. 2.8(b)]. The number of times Σ covers the unit sphere gives the topological charge. Topological charge q is of integer value $0, \pm 1, \pm 2, \dots$



Figure 2.8: (a) Mappings Σ that cover S^2 only partially correspond to topologically unstable defect configurations as they can be contracted into a point in the order parameter space. (b) Mappings Σ that fully cover S^2 characterize stable topological defects.

There is a continuous infinity of director configurations for each value of the hedgehog charge. In the simplest unit charge hedgehog configuration, shown in Fig. 2.9(a), the director points radially outward from the point core like the electric field near a point charge. This configuration is called a radial hedgehog for obvious reasons. Other configurations can be obtained from the radial configuration via rotations through arbitrary angles about any axis. Two examples are shown in Fig. 2.9(b, c). When the director of a radial hedgehog is rotated about a fixed axis through π , a hyperbolic hedgehog, shown in Fig. 2.9(c), is produced. The hyperbolic hedgehog can be obtained via a series of continuous distortions of the director passing through intermediate configuration, such as the circular configuration shown in Fig. 2.9(b). Thus, radial, hyperbolic and all intermediate hedgehogs are topologically equivalent [131]. The director profile for the three configurations, shown in Fig. 2.9, can be constructed in a coordinate frame (x, y, z) from symmetry arguments:

$$\mathbf{n}_{rad} = \frac{(x, y, z)}{r}, \quad \mathbf{n}_{circ} = \frac{(y, -x, z)}{r}, \quad \mathbf{n}_{hyp} = \frac{(-x, -y, z)}{r}, \quad (2.28)$$

where $r = \sqrt{x^2 + y^2 + z^2}$. Generally, point defects with the same magnitude of the topological charge are energetically not equivalent. Using Eq. (2.28), the elastic free energy F of the three configurations can be calculated by integrating f_E^{FO} (omitting K_{13} and K_{24}) [131]:

$$F_{rad} = 8\pi K_{11} R, \quad (2.29)$$

$$F_{circ} = \frac{8\pi}{15} (2K_{11} + 5K_{22} + 3K_{33}) R, \quad (2.30)$$

$$F_{hyp} = \frac{8\pi}{15} (3K_{11} + 2K_{33}) R, \quad (2.31)$$

where R is the size of the liquid crystal volume. Relative energies of the three configurations depend on the exact values of the elastic constants. Nevertheless, the bend elastic constant K_{33} is typically the largest, making circular hedgehog generally the one with the highest energy. To estimate the energy of point defects we take $K_{11} \sim 10^{-11}$ N and $R \sim 10$ nm, which yields for the radial point defect $F_{rad} \sim 600 k_B T$. The value of F_{rad} is substantially above unity, which shows that point defects are unable to form spontaneously by simple thermal fluctuations in an equilibrated nematic.

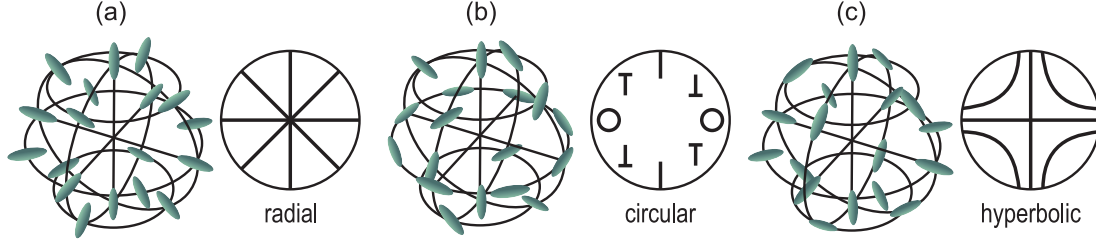


Figure 2.9: (a) A radial hedgehog in which the director points radially outward from a central point like the electric field of a point charge. (b) A circular hedgehog obtained from a radial hedgehog by rotating the director at every point through $\frac{\pi}{2}$ about the vertical axis. (c) A hyperbolic hedgehog obtained from the radial hedgehog by rotating the director at every point by π about the vertical axis. In each case the figures at the left provide a three-dimensional depiction of the defect, whereas that at the right show a projection onto any plane containing the polar axis. In (b), standard notation in which the nail heads indicate the end of the director coming out of the plane, is used. Adapted from Ref. [131].

Point defects have an internal structure of their core region, which depends on material properties of the liquid crystal. Three types of the core structures are found: (i) isotropic melted core [139], (ii) core with a small defect ring [140] and (iii) split-core configuration [141]. The structures are (meta)stable one with respect to another, with the relative energies depending primarily on the ratio of the elastic constants L_2/L_1 [142]. The transition between configuration (i) and (ii) is discontinuous [141] and the radius of the small defect ring in configuration (ii) increases with the ratio L_2/L_1 and with temperature approaching nematic-isotropic transition value. Approximate analytical formalism can be found in [140,141].

Defect loops and point defects are topologically equivalent or homotopic, as they can be continuously transformed one into another. Disclination loops can be surrounded by a closed surface, denoted by σ , which is different if compared to lines. The director profile on σ , just as for point defects, determines the topological charge q of the loop as its global topological property. Locally, however, the winding number k can be used to characterize the symmetry of the director, surrounding the defect line.

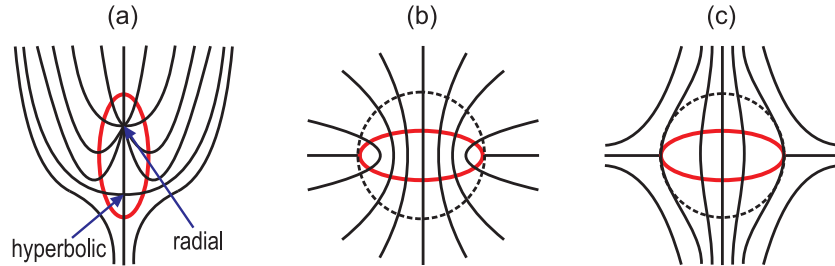


Figure 2.10: (a) Radial and hyperbolic hedgehog combining to give a configuration with zero net charge. Disclination rings with unit hedgehog charge: (b) radial and (c) hyperbolic hedgehog. The dotted line in each image represents a sphere beyond which the director configuration is that of a hedgehog. Adapted from Ref. [131].

Topological invariants have to be preserved in annihilation or creation of defects, therefore whenever a defect is introduced into an uniformly ordered nematic, it is compensated by the

defect of the opposite sign. Figure 2.10(a) shows how radial and hyperbolic hedgehogs can combine to give a zero net charge configuration: $|-1 + 1| = 0$. Figure 2.10(b, c) depicts disclination rings with far-field director configurations corresponding to radial and hyperbolic unit charge hedgehogs. These rings can be shrunk to a point, generally observed in experiments, due to the limited resolution of the optical microscope.

One should stress that topological summation rules for the total winding number k_t and the total topological charge q_t have to be introduced in accordance with the chosen definitions for the sign of the winding number and charge. In non-uniform geometries the total winding number k_t and the total topological charge q_t are determined by the anchoring properties of the confining surfaces. For example, a homeotropic spherical droplet has $q_t = 1$ [143].

Colloidal inclusions effectively act as point defects with their surface anchoring and their shape determining their topological charge. Spherical particles with the surface favoring either homeotropic or planar orientation carry topological charge $+1$ each. For N such particles in a uniform geometry the total charge of the compensating defects has to be equal to $-N$. The universality of this rule allows for compensating the topological charge of several particles with a single defect of larger topological charge or several separate defects of lower topological charges. This universality will be the main element of understanding entangled, non-singular and knotted defect configurations, explicitly described in Chapters 4 and 5.

2.6 Multipole expansion approach and interparticle potentials

Director profile surrounding colloidal particles in a uniform field can not be found analytically because of the highly nonlinear Euler-Lagrange equations governing the nematic elasticity. The nonlinearity of the nematic is pronounced at most close to the particle walls, where spatial gradients of the director are large. Omitting this region by properly incorporating only the far-field behavior of the nematic, where spatial gradients are small, one can however linearize Euler-Lagrange equations and find analytical solutions for the director in terms of elastic multipoles [21,131].

Multipole expansion approach assumes approximately uniform director $\mathbf{n}(\mathbf{r}) = (n_x, n_y, 1)$, where $n_x \ll 1$ and $n_y \ll 1$ are considered as small perturbations. Using n_x and n_y , the nonlinear Frank's one constant elastic free energy [Eq. (2.13)] can be replaced by the harmonic free energy density f_E^H :

$$f_E^H = \frac{1}{2}K \sum_{\mu=x,y} (\nabla n_\mu)^2. \quad (2.32)$$

The Euler-Lagrange equations, calculated for this free energy, are Laplace equations $\nabla^2 n_\mu = 0$. For large coordinate vector $\mathbf{r}$ from the center of the particles the solution of Laplace equation can be constructed with multipole expansion [131]:

$$n_\mu = \frac{A^\mu}{r} + \frac{\mathbf{p}^\mu \cdot \mathbf{r}}{r^3} + \frac{c_{ij}^\mu x_i x_j}{r^5} + \dots, \quad \mu = x, y, \quad (2.33)$$

where A^μ , $\mathbf{p}^\mu$, c_{ij}^μ are expansion coefficients and x_i are Cartesian coordinates of the position vector $\mathbf{r}$. The director field around the spherical particle should be invariant with respect to rotations about the far-field director $\mathbf{n}_0 = (0, 0, 1)$, which sets the monopole coefficient $A^\mu = 0$. The dipolar part of the expansion should change sign if the companion defect shifts from above to below the particle. Such requirement gives together with the rotational invariance:

$$\mathbf{p}^\mu = (\mathbf{p} \cdot \mathbf{n}_0) \mathbf{e}^\mu, \quad (2.34)$$

$$c_{ij} = c(n_{0i} e_j^\mu + e_i^\mu n_{0j}), \quad (2.35)$$

where $\mathbf{e}^\mu$ is the unit vector along $\mu = x, y$. Vector $\mathbf{p}$ is the dipole moment of the director pointing from the companion defect to the center of the particle and c is the magnitude of the

quadrupolar moment. Using dimensional analysis, one finds $p \propto d^2$ and $c \propto d^3$, where d is the diameter of the particle. Finally, for $\mathbf{n}_0 = (0, 0, 1)$ director component n_μ is written in terms of multipoles as:

$$n_\mu = p_z \frac{\mu}{r^3} + 2c \frac{z\mu}{r^5}, \quad \mu = x, y. \quad (2.36)$$

The far-field solutions for the director around a homeotropic particle can also be found using electrostatic analogy, for instance, a conducting sphere with a reduced charge P exposed to an uniform external electric field of roughly unit strength $\mathbf{E}_{dir}$. Electric field at position $\mathbf{r}$ for a conducting sphere with diameter $d = 2r_c$ and the symmetry axis along z reads as [21,131]:

$$\mathbf{E}_{dir} = \mathbf{e}_z + Pr_c^2 \frac{\mathbf{r}}{r^3} - r_c^3 \frac{r^2 \mathbf{e}_z - 3z\mathbf{r}}{r^5}, \quad (2.37)$$

where $\mathbf{e}_z$ is unit vector along coordinate axis z . The electrostatic analog assigns the dipole moment Pr_c^2 and the quadrupole moment $\frac{3}{2}r_c^3$ to the particle. Here the charge P should be considered as the variational parameter for the director, which determines the distance from the center of the particle to the companion hyperbolic hedgehog defect r_d . Using one elastic constant approximation for the director free energy minimization, hyperbolic defect position is found at $r_d = 1.17r_c$ ($P = 3.08$) [21]. Normalized dipolar and quadrupolar electric fields $\mathbf{E}_{dir}/|\mathbf{E}_{dir}|$ are separately visualized in Fig. 2.11(a, b), respectively.

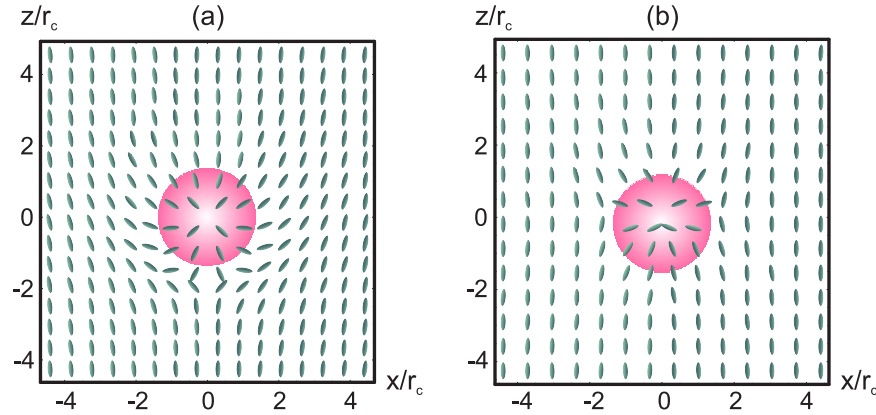


Figure 2.11: Multipole expansion results: (a) dipolar director field $\mathbf{E}_{dir}^D = \mathbf{e}_z + 3.08r_c^2 \mathbf{r}/r^3$ and (b) quadrupolar director field $\mathbf{E}_{dir}^Q = \mathbf{e}_z - r_c^3(r^2 \mathbf{e}_z - 3z\mathbf{r})/r^5$. Note that both $\mathbf{E}_{dir}^D$ and $\mathbf{E}_{dir}^Q$ have to be normalized and that shaded region presents the size of colloidal particle for calculated director field.

The interparticle potentials can be analytically calculated within the multipole expansion approach. It is assumed that particle separations are large enough for the director around the particles to retain the dipolar or quadrupolar multipole structure. Particle interaction is then based on the over-lapping of far-field deformation areas induced by particles, where the changes in the elastic energy of the orientational order within the over-lapping regions drives the particles. Formal calculation of the dipole-dipole (PP), quadrupole-quadrupole (CC) and dipole-quadrupole (PC) interparticle potential U can be found in [21], as here we present only the results. Elastic potential $U(\mathbf{R})$ between two particles at positions $\mathbf{r}$ and $\mathbf{r}'$ ($\mathbf{R} = \mathbf{r} - \mathbf{r}'$), with respective dipole and quadrupole moments p , p' , c , and c' , equals:

$$U(\mathbf{R}) = 4\pi K \left[pp' V_{PP}(\mathbf{R}) + \frac{4}{9} cc' V_{CC}(\mathbf{R}) + \frac{2}{3} (cp' - c'p) V_{PC}(\mathbf{R}) \right]. \quad (2.38)$$

The interaction terms are defined as follows:

$$V_{PP}(\mathbf{r}) = \frac{1}{r^3}(1 - 3\cos^3\theta), \quad (2.39)$$

$$V_{CC}(\mathbf{r}) = \frac{1}{r^5}(9 - 90\cos^2\theta + 105\cos^4\theta), \quad (2.40)$$

$$V_{PC}(\mathbf{r}) = \frac{1}{r^4}(15\cos^3\theta - 9\cos\theta), \quad (2.41)$$

with θ being the angle between $\mathbf{r}$ and the far-field director $\mathbf{n}_0$. The compact formula for the interparticle potential in Eq. (2.38) uses the following assumptions and approximations: (i) director is roughly uniform $\mathbf{n} = (n_x, n_y, 1)$; $n_x, n_y \ll 1$, (ii) particles interact in a bulk nematic, (iii) particles carry only an elastic dipole and quadrupole, (iv) particle separation is large enough for the director to remain in the dipolar or quadrupolar configuration. Interestingly, despite strong constraints on the validity of the above multipole interparticle potentials, they give qualitatively proper spatial profiles and power law dependence, as shown in experiments [33,52,78,136].

Experiments measuring the interparticle potentials are typically performed in the geometry of a cell using a combination of opto-magnetic tweezers and video microscopy. It is important to note here that the power law behavior of the elastic potential [Eqs. (2.39)-(2.41)] is expected only in a limited intermediate range of the interparticle separations. At close separations the particles can induce strong director deformation, which breaks the multipole structure of the director, and the interparticle potential is determined primarily by the local surface effects. At larger particle separations, comparable to cell thickness, the confining substrates impose their own order, which effectively reduces the effect of inclusions on the director. The long range of the particle-induced deformation is thus suppressed (screened) and decays exponentially with cell thickness as a typical length scale [53,144,145]. Since director deformations are the cause for the interparticle forces, exponential decay is expected also in the force profile. Similar screening effects were extensively studied in the defect annihilation processes [146–148].

2.7 Short introduction to knot theory

2.7.1 Historical account

Knots are ubiquitous topological objects, symbols of complexity, that have fascinated people from the dawn of human history. Initially, the interest in knots came out of practical needs, especially those of builders, sailors and weavers. Over the centuries they found a plethora of useful applications, such as tying objects, braiding hair, weaving clothes or rugs, fastening animals and securing surgical sutures [149]. Knotted strings, known as *kipu*, were used by the Inca civilization for record-keeping and even communication [150]. Utilitarian and technological considerations aside, knots also have an aesthetic and magical aspects that have inspired artists to design entangled patterns in Celtic artwork, jewelry and medieval architectural decoration [151].

Equally important, knots are scientifically appealing and have attracting increasing attention ever since the beginnings of the mathematical theory of knots that started in the 19th century. The possibility to study knots from the topological point of view was for the first time proposed by Carl Friedrich Gauss [150]. He formulated the ‘crossing problem’ by assigning letters to the crossing points on a self-intersecting system of linked circular wires and he was trying to determine ‘words’ defining a closed curve in 1794. Gauss’ student Johann Benedict Listing also studied knots and was the one who coined the word *topology*. The main stimulus for the classification of knots came in the 1860s when Lord Kelvin attempted to deduce the structure of the periodic table of the elements by assuming that atoms were actually linked or knotted vortices in the ether [152]. His friend and colleague Peter Guthrie Tait was motivated by this notion and led by true pioneering spirit he started to create the first table of alternating knots [152]. Another colleague of Kelvin and Tait, James Clerk Maxwell, had also developed a strong interest in knots

and studied them in terms of electromagnetic theory [153]. Nowadays, these achievements can rightfully be considered as the genesis of knot theory.

Although Lord Kelvin's theory fell into disfavor, it stimulated interest in the subject. Today knots are encoded in the foundations of many scientific fields, including polymer physics [154,155], statistical mechanics [156,157], biochemistry [158] and biophysics [159–161]. Knotting and catenation of DNA molecules occur in living cells and viruses during the processes of replication, transcription and recombination, which play an essential role in the evolution of life [162,163]. The biological solution to this entanglement problem is the existence of enzymes *topoisomerases* and *recombinases* which, in order to mediate these vital life processes, manipulate cellular DNA in topologically interesting and non-trivial ways. In modern physics, knot-like structures have been studied in classical field theory [164], Bose-Einstein condensates [165], chiral spin states of topological insulators [166–168], non-Abelian states of matter [169,170] and optics, where linked and knotted beams of light [171–173] have been demonstrated recently. However, relatively few experimental realizations of knots in condensed matter physics have been reported so far.

2.7.2 Fundamental concepts

Within knot theory, which is a branch of topology, a *knot* is defined as a closed, non-self-intersecting elastic curve, embedded in three-dimensional (3D) space [151]. The simplest trivial knot is a circle, known as *unknot*, whereas two or more disjoint circles are called *unlink*. The simplest non-trivial knot is the *trefoil* or clover-leaf knot, whereas the simplest non-trivial link, known as the *Hopf link*, is composed of two interlocked rings, each independently unknotted. In general, a *link* is a collection of knots which do not intersect, but which may be linked together [151]. To simplify the terminology, we will often refer to links as knots and use the term *proper knot* when specifically referring to a single component knot. Examples of several most known knots and links are collected in Fig. 2.12.

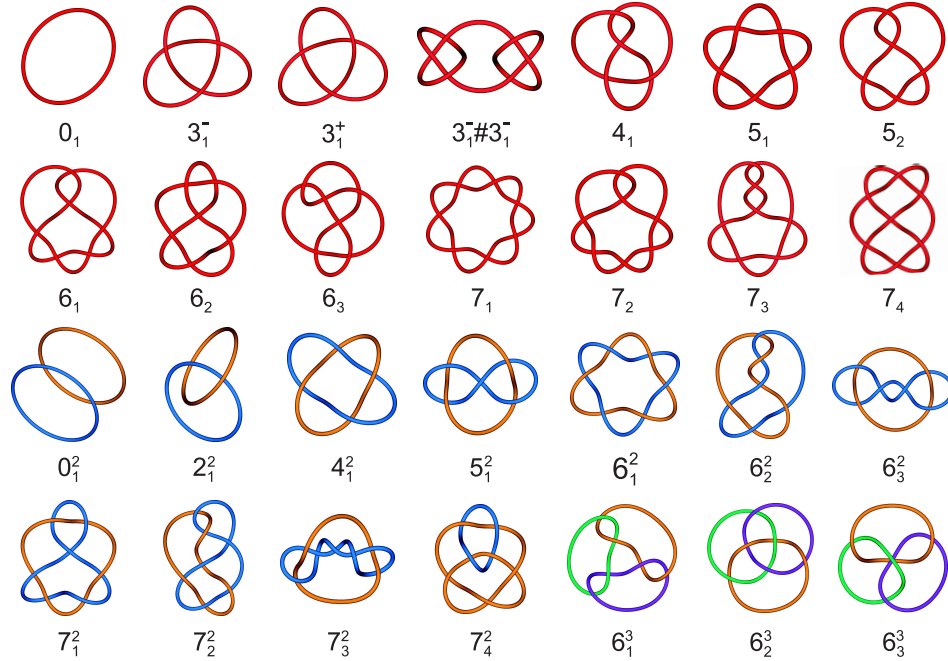


Figure 2.12: Knot and link diagrams. Throughout this Section we adopt Rolfsen knot type notation C_α^n [174]. Examples include: trivial knot or unknot 0_1 , left-handed trefoil 3_1^- , right-handed trefoil 3_1^+ , granny knot $3_1^- \# 3_1^-$, figure-8 knot 4_1 , pentafoil knot 5_1 , three-twist knot 5_2 , Stevedore knot 6_1 , Miller institute knot 6_2 , knot 6_3 , septafoil knot 7_1 , knots 7_2 and 7_3 , endless knot 7_4 , trivial link or unlink 0_1^2 , Hopf link 2_1^2 , Solomon link 4_1^2 , Whitehead link 5_1^2 , Magen David link 6_1^2 , two-component links 6_2^2 , 6_3^2 , 7_1^2 , 7_2^2 , 7_3^2 , 7_4^2 , closed three-link chain 6_1^3 , Borromean rings 6_2^3 and three fibers in the Hopf fibration 6_3^3 .

Two knots are *equivalent* and have the same *knot type* if one knot can be smoothly deformed to become the other, no matter how the knot is stretched or twisted without being cut [151]. A natural way to look at knot equivalence is by examining a projection of the knot onto a plane. Such a projection, called a *knot diagram* or *presentation*, can always be made so that the cross-over points have one of the two forms shown in Fig. 2.13(a). It was shown by Kurt Reidemeister as early as 1927 that two knots are equivalent if and only if the projection of one can be converted into the projection of the other through the use of just three types of moves, along with continuous deformations of the knot diagram in the plane [151]. The three *Reidemeister moves* are illustrated in Fig. 2.13(b). Using the Reidemeister moves it is clear that any knot has an infinite number of distinct projections in the plane, of arbitrary complexity. For this reason, knot diagrams are often drawn in a form that has the fewest crossings of all possible projections. Such a knot diagram is called *ideal* or *minimal projection* of the knot and the number of crossings in diagrams of the form shown in Fig. 2.12 is called the *crossing number*. The crossing number of the minimal projection of the knot also provides an intuitive measure of complexity and it has been the custom to rank knots in catalogues according to their crossing numbers [151]. For these purposes, it is necessary to list only *prime* knots. These are knots that cannot be subdivided into two or more simpler non-trivial knots. Knots and links that are not prime are called *composite*, as they correspond to the operation of tying two separate knots sequentially in a piece of elastic curve. All prime knots and links in a minimal projection with nine or fewer crossings are gathered in Rolfsen's book [174]. This most well-known knot catalogue uses a standard naming convention, where knots are named according to their minimal crossing number C with a subscript α indicating the cardinal index used to distinguish among knots with the same crossing number. For multi-component links, a superscript n indicates the number of distinct components in the link. An example is the Hopf link $C_\alpha^n = 2_1^2$, which is the only knot or link with a crossing number two.

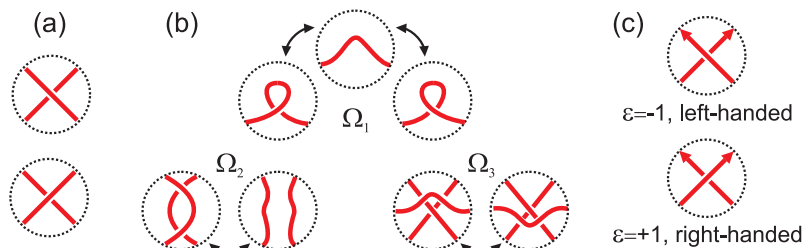


Figure 2.13: (a) Crossings permitted in planar projections. (b) Reidemeister moves, denoted by the symbols Ω_1 , Ω_2 , Ω_3 , refer to local moves of knot diagram that do not change the knot type. The moves that they allow are the following: Ω_1 - twist and untwist in either direction, Ω_2 - move one string completely over another, Ω_3 - move a string completely over or under the crossing. (c) Oriented crossing types ε , used for computing the writhe and the linking number. Sign convention states that negative or left-handed crossing is denoted by $\varepsilon = -1$ and positive or right-handed crossing is denoted by $\varepsilon = +1$, respectively. Adapted from Ref. [149].

Although mathematicians are not concerned with mirror images when constructing knot catalogues, it is useful to have a notation for the mirror image of a given knot. The left and right-handed trefoils, shown in Fig. 2.12, are denoted as 3_1^- and 3_1^+ , respectively. Most knots are not equivalent to their mirror images and they are known as *chiral*. Some knots, such as figure-8 knot 4_1 , are *achiral*. Chirality can be important when forming composite knots. The granny knot $3_1^- \# 3_1^-$, illustrated in Fig. 2.12, is the connected sum of two left-handed trefoils.

2.7.3 Topological invariants

One of the basic questions in knot theory is to find an algebraic way of distinguishing a knot from the unknot or distinguishing two knots from one another. The idea is to find a *knot invariant*

in such a way that the value of the invariant depends on the knot type but not on its particular embedding in space. Useful examples of knot invariants are number of closed loops, referred to as components, crossing number in minimal projection and *linking number* [151]. The linking number can be defined for *oriented* links as the half sum of the signs over all crossings between two different components (self-crossings are ignored), where left-handed crossing scores as -1 and right-handed as $+1$ [see Fig. 2.13(c)]. A particular component may be given an orientation by assigning a direction, denoted by an arrow, in which to travel along the entire knot projection. Reversing the orientation on one component changes the sign of the linking number. Another useful definition is the *writhe number* of a given oriented curve, which is defined in a similar manner to the linking number, except that sum of the signs over all crossings is considered. Note that writhe number is not a knot invariant but just a property of an oriented knot diagram, as its sign characterizes the topological chirality.

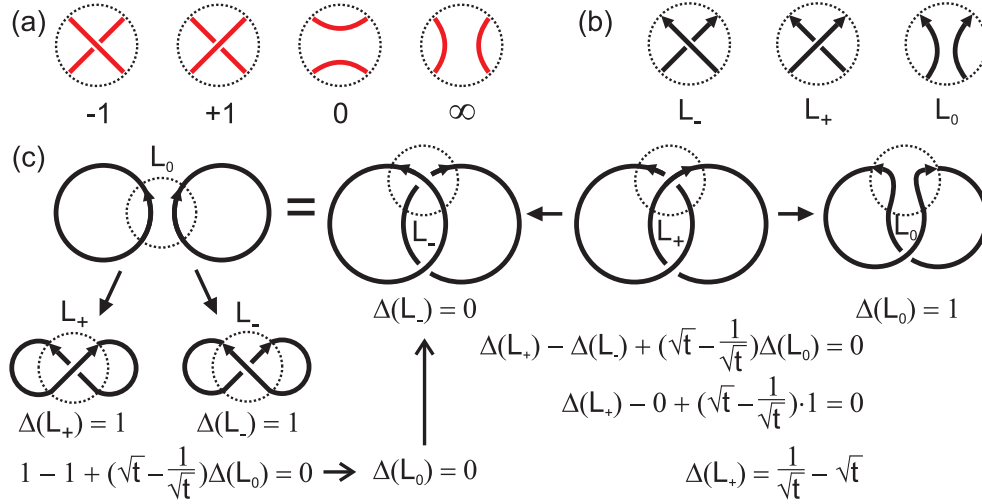


Figure 2.14: (a) Conway trivial tangles, which serve as the building blocks of any alternating knot projection and can be used for advanced algebraic operations on knot diagrams. (b) Oriented tangles appearing in skein relation. (c) Example of computing the Alexander polynomial for the unlink (left) and the Hopf link (right). Adapted from Ref. [175].

However, the quoted knot invariants are rather weak and not complete, therefore more extensively knotted systems require more powerful techniques of knot classification. One ingenious strategy for distinguishing knots is to transform a knot projection into a special polynomial formula. The first knot polynomial was discovered by James Alexander in 1928 [151,176]. The polynomial is denoted by $\Delta(t)$ and it is constructed according to numbers of different kinds of crossings in a knot diagram, which can have both positive and negative powers of t . As an example, a trefoil knot has $\Delta(t) = t - 1 + t^{-1}$. Mathematicians were using the *Alexander polynomial* to distinguish knots and links for the next 60 years. Then, in 1969, John Horton Conway invented simpler way to calculate the Alexander polynomial using a so-called *skein relation* [177]. It is based on the idea of *tangles* or sections of a knot diagram, consisting of two separate strings with open ends, illustrated in Fig. 2.14(a). The trivial tangles, denoted by $+1$, -1 , 0 and ∞ , may be changed and combined using the algebraic operations to produce more complex tangles and following the simple manipulation of the tangle strings a powerful notation system with efficient enumeration has been established as well [151,177]. The skein relation starts with three *oriented tangles*, denoted by L_- , L_+ and L_0 , that differ only locally in the region of one crossing, as shown in Fig. 2.14(b). The skein relation for the Alexander polynomial states that:

$$\Delta(L_+) - \Delta(L_-) + \left(\sqrt{t} - \frac{1}{\sqrt{t}}\right) \Delta(L_0) = 0. \quad (2.42)$$

Together with the fact that the unknot has $\Delta(t) = 1$ by definition, this skein relation makes it possible to calculate $\Delta(t)$ for any knot or link. The simplest non-trivial calculation of two unknotted loops is presented in Fig. 2.14(c). The formula above specifies how the Alexander polynomials of each of these loops are related. Calculating the polynomial for a given knot involves the repetitive application of the skein relation until one is left with a collection of unknots or other knots whose polynomials have been determined previously [151,176]. At each step, any sequence of Reidemeister moves is allowed. Such a procedure results in a *resolving tree* [151], an example of which is shown in Fig. 2.14(c) for the Hopf link. The leaves of this tree are all unknots with a known polynomial. Working back toward the root of the tree and applying the skein relation allows one to compute the Alexander polynomial of the original knot.

It turns out that the Alexander polynomial is a reasonably powerful knot invariant with several deficiencies; it is immune to mirror images and not always correct for the composite knots [178]. However, for the most of the history of knot theory it was the only knot polynomial. Therefore, it was quite a shock when Vaughan Jones discovered a powerful new polynomial invariant for knots and links in 1985, defined by the skein relation [175,179]:

$$\frac{1}{t}V_{L_+}(t) - tV_{L_-}(t) = \left(\sqrt{t} - \frac{1}{\sqrt{t}}\right)V_{L_0}, \quad V_{\text{unknot}}(t) = 1. \quad (2.43)$$

The *Jones polynomial* $V(t)$ is far more discriminating than the Alexander polynomial $\Delta(t)$. For example, it is able to distinguish the two versions of the trefoil; the left and right-handed trefoils having Jones polynomials $-t^{-4} + t^{-3} + t^{-1}$ and $t + t^3 - t^4$, respectively. These two polynomials illustrate a general feature of the Jones polynomial, the possibility to find the mirror image of a given knot by making the substitution $t \rightarrow \frac{1}{t}$. In the case of the trefoil and many other knots, this property provides an easy proof of knot chirality [178].

Jones' discovery, awarded by the famous Fields medal in 1990, had a profound effect on the knot theory community, causing researchers to start looking for even more accomplished polynomial invariants. Remarkably, six researchers working independently in four groups almost simultaneously came up with the new generalized polynomial, called HOMFLY polynomial after the initials of its discoverers (Hoste, Ocneau, Millet, Freyd, Lickorish and Yetter) [151]. Since then, many other knot polynomials have been discovered, however, we are still lacking the perfect description of knots. Thus, we continue with a discussion of the Jones polynomial as understood by Louis Kauffman. In order to define the Jones polynomial, he has developed the *Kauffman polynomial*, denoted by $X(K)$, where K designates knot, which has shown much simpler approach to calculate the Jones polynomial [151,156]. It has double advantage of being very easy and of clearly showing the relationship of the polynomial with statistical physics [156]. Kauffman introduced its construction by the so-called *states model* [149,156]. The model works by eliminating all the crossings in a knot, replacing the knot with disconnected circles. Each crossing may be thus replaced by one of two states (horizontal A -split or vertical A^{-1} -split), which determines the way it will be eliminated, while all possible combinations of crossing states then determine a state of the knot as a whole (see Fig. 2.15). Kauffman onward defined the *bracket polynomial* $\langle K \rangle$ of a single variable A as a sum over all 2^n states of the knot:

$$\langle K \rangle = \sum_{S_i} \langle S_i | K \rangle (-A^2 - A^{-2})^{|S_i|-1}, \quad (2.44)$$

where $\langle S_i | K \rangle$ denotes the product of all A and A^{-1} at the crossings and $|S_i|$ represents the number of unknotted circles in the resulting link diagram. Since there are n crossings and one has two choices of how to split each crossing, there are exactly 2^n links. Equation (2.44) thus establishes not only the uniqueness of the bracket polynomial $\langle K \rangle$, but its existence as well. As an example, the calculation of the bracket polynomial for the figure-8 knot is explicitly presented in Fig. 2.15.

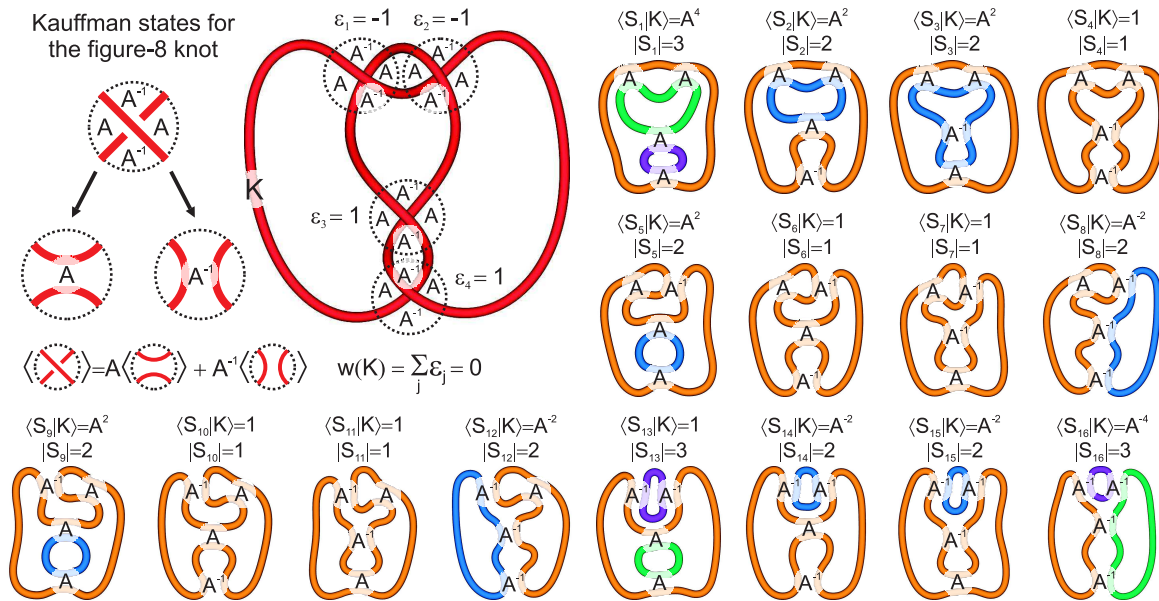


Figure 2.15: Kauffman states and bracket polynomial for the figure-8 knot. Each crossing ε_j may be smoothed in one of two states, A or A^{-1} , and all possible combinations of crossing states determine a state of the knot as a whole. The writhe number $w(K)$ is calculated as a sum of all crossing numbers ε_j . The bracket polynomial $\langle K \rangle$ is calculated as a sum over all $2^4 = 16$ states of the knot, where 4 denotes the number of crossings; $\langle S_i | K \rangle$ denotes the product of all A and A^{-1} at the crossings and $|S_i|$ corresponds to the number of circles in the resulting link diagram [175].

Hence follows:

$$\begin{aligned}
 \langle K \rangle &= A^4(-A^2 - A^{-2})^2 + A^2(-A^2 - A^{-2}) + A^2(-A^2 - A^{-2}) + 1 + A^2(-A^2 - A^{-2}) + 1 + 1 \\
 &+ A^{-2}(-A^2 - A^{-2}) + A^2(-A^2 + A^{-2}) + 1 + 1 + A^{-2}(-A^2 - A^{-2}) + (-A^2 - A^{-2})^2 \\
 &+ A^{-2}(-A^2 - A^{-2}) + A^{-2}(-A^2 - A^{-2}) + A^{-4}(-A^2 - A^{-2})^2 \\
 &= A^8 - A^4 + 1 - A^{-4} + A^{-8}.
 \end{aligned} \tag{2.45}$$

Unfortunately, it turns out that the bracket polynomial is not invariant under the first Reidemeister move Ω_1 [149]. Therefore, in order to define the Kauffman polynomial, which is a knot invariant, one has to define it by writing

$$X(K) = (-A)^{-3w(K)} \langle |K| \rangle, \tag{2.46}$$

where $w(K)$ is the writhe number of oriented knot diagram K and $\langle |K| \rangle$ is the bracket polynomial of non-oriented knot diagram $|K|$, obtained from the oriented one by neglecting its orientation [149]. Kauffman's trick is the factor $(-A)^{-3w(K)}$, which removes the coefficient $A^{\pm 3}$ resulting from Reidemeister move Ω_1 . Finally, the Jones polynomial $V(t)$ is obtained from the Kauffman polynomial $X(K)$ simply by using the substitution $A = t^{-\frac{1}{4}}$ [149,156].

2.7.4 Connection with statistical mechanics and planar graphs

The discovery of Jones and Kauffman polynomials extends far beyond the scope of knot theory and it is popular because of its connections to other branches of mathematics (braid theory, algebra of operators) and especially to physics (statistical models, quantum groups and biophysical systems) [149]. Over the past two decades there has been a remarkable interplay between ideas in statistical mechanics and the construction of new invariants of knots [156]. Statistical models deal with regular structures made up of atoms with spins that have simple local interactions, symbolized by the line segments joining the interacting atoms. Such a system K must have a

partition function $Z(K)$, which is the sum over all possible states of K of certain expressions that depend on the energies of local interactions. This function permits one to calculate the principal global parameters of the systems (temperature, total energy) and to study the phase transitions such as passage from the liquid to the solid state. It is thus interesting and surprising that a kind of partition function allows us to define and to calculate the Jones polynomials for knots [151,156,175].

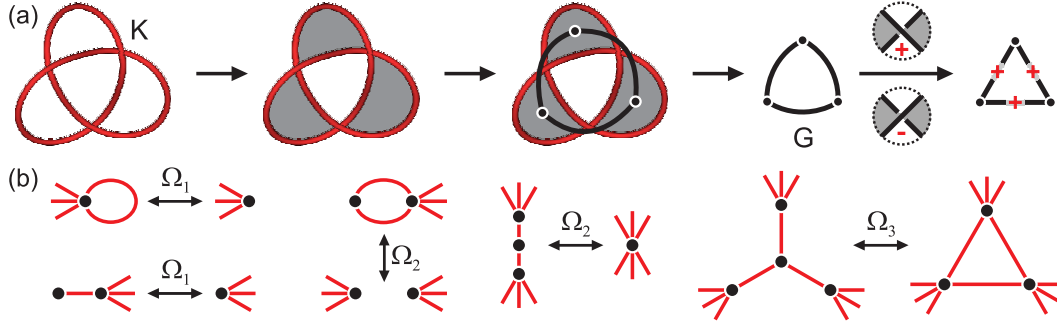


Figure 2.16: (a) Planar graph G of a knot can be extracted from the knot diagram K by alternately painting in grey and white the parts of the plane delimited by the knot projection, taking the grey regions for the vertices of the graph and joining them by an edge if the grey regions possess a common crossing. A signed planar graph is obtained according to sign convention. (b) Reidemeister moves Ω_1 , Ω_2 and Ω_3 on planar graphs; Ω_3 yields the star-triangle exchange [151].

The first step in making the connection between knot theory and statistical mechanical models is to shade the regions of a knot diagram K like a checkerboard. Then one can extract a planar graph G by taking the shaded regions as vertices (or atoms of the model) and the crossings as edges (interactions), as illustrated in Fig. 2.16(a). Moreover, the edges can be given positive or negative signs according to the relative orientation between the crossing and the checkerboard pattern. Next, one has to define the state of the system as an arbitrary function that assigns a spin to each atom and the spin can take only two values (up or down). When the spin model is in a well-determined state $s \in S$, here S denotes the set of all possible states, the local interaction energy $E[s(\nu_1), s(\nu_2)]$ of the two vertices joined by the edge $[\nu_1, \nu_2]$ is assumed to be equal to ± 1 if they have the same spin and to $A^{\pm 1}$ if the spins are opposite. The plus or the minus sign is chosen depending on whether the edge is positive or negative and $A^{\pm 1}$ are the variables of the polynomial that we want to obtain. That done, we can define the partition function of the spin model by the equation:

$$Z(K) = \frac{1}{\sqrt{2}} \sum_{s \in S} \prod_{[\nu_i, \nu_j] \in M} E[s(\nu_i), s(\nu_j)], \quad (2.47)$$

where M is the set of all edges. It is now obvious that the partition function depends simply on the sum over all states of the spin model's energy function. That is, each state defines the spins of all the vertices in the graph and thus the energy of the interactions between them. The value of the partition function should not essentially change if a Reidemeister move is applied to the underlying knot diagram. Moreover, it has been proved that the energy functions of spin models that satisfy the star-triangle relation and other relations corresponding to the other Reidemeister moves [see Fig. 2.16(b)] will yield partition functions that are also invariants of knots [149,151]. The Ising model, for instance, yields an invariant known as the Arf invariant [175]. Finally, deriving the Jones polynomial from the partition function requires applying to it a variation of Kauffman's trick, described above.

More information about the knot theory can be found in several excellent textbooks that discuss the topic in great detail [150,151,156,174,178,180], as well as in popularized accounts intended for a non-mathematical audience [149,175,181].

Materials and experimental techniques

An important part of the experimental work related to preparation and characterization of the colloidal structures was performed using the optical tweezers and observation of the assembled structures with polarizing optical microscopy over a wide range of experimental conditions. The present Chapter describes materials, principles and procedures of the experimental techniques employed for the study of samples. This includes preparation of colloidal dispersions and liquid crystal cells, methods of optical microscopy, brief theory of operation and a basic design of optical tweezers, optical trapping and measurement of interparticle forces in an anisotropic solvent. Instead of repeating tedious texts onwards, we list them here for easy reference.

3.1 Materials and sample preparation

3.1.1 Liquid crystalline and colloidal material

A single component liquid crystal, 4-cyano-4'-pentyl-1,1'-biphenyl, also well-known under the commercial names 5CB or K15, was employed throughout presented research. It is one of the most common nematic liquid crystals, often used in mixtures in the LCD industry. The material was purchased from Merck (Germany) and used as received without further purification. The structural formula of 5CB molecule and a fresh sample are presented in Fig. 3.1. The molecule consists of a long flexible carbo-hydrate chain on one side of two consequently bonded phenyl rings and a polar CN group on the other side. The alkyl-cyano-biphenyl molecules are strongly polar and have a strong tendency to form dimers in order to minimize the dipolar energy. Depending on the length of the carbon-hydrate chain, the *n*-alkyl-cyano-biphenyl materials form different phases and thus exhibit different phase diagrams. The phase sequence of 5CB on cooling follows the order: isotropic (*I*) → nematic (*N*) → crystal (*C*). The temperatures and enthalpies of the phase transitions are presented in Table 3.1 [182].

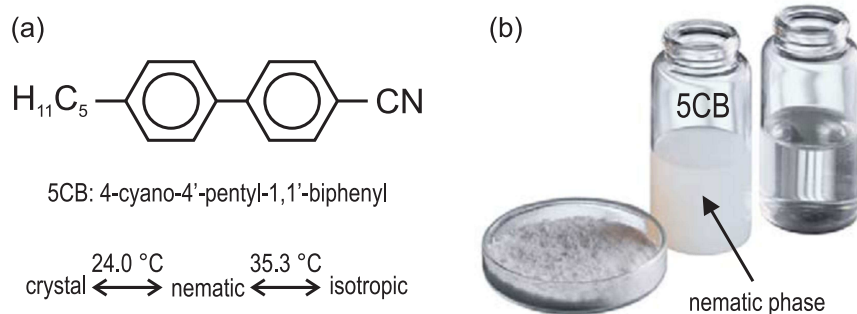


Figure 3.1: (a) Structural formula of 4-cyano-4'-pentyl-1,1'-biphenyl liquid crystal. The molecule consists of a rigid backbone formed by two benzene rings and a polar CN group attached to the aromatic ring. (b) Sample of 5CB in crystal, nematic and isotropic phase. Adapted from Ref. [183].

Material	M [g/mol]	$\rho(I)$ [kg/m ³]	$T(C \rightarrow N)$ [°C]	ΔH [10 ⁶ J/m ³]	$T(N \rightarrow I)$ [°C]	ΔH [10 ⁶ J/m ³]
5CB	249.359	1002.4	24.0	68.5	35.3	1.56

Table 3.1: The liquid crystal material used in the study, its molecular mass M , density in the isotropic phase $\rho(I)$, temperatures T and enthalpies ΔH of the phase transitions. Values are taken from [182].

Optical and elastic properties of used liquid crystal are collected in Table 3.2.

Material	T [°C]	$\epsilon_{ }$	$\epsilon_{\perp}$	n_e	n_o	Δn	K_{11} [pN]	K_{22} [pN]	K_{33} [pN]
5CB	29.0 (N)	17.9	7.2	1.719	1.535	0.184	6.4	3.2	10
	36.0 (I)	10.5	10.5	1.65	1.65	0	4.9	2.0	4

Table 3.2: Static dielectric constant ϵ , optical refractive index n , birefringence Δn and three main elastic constants K_{11} , K_{22} , K_{33} of 5CB liquid crystal in the nematic and the isotropic phase [182,184,185].

Material	Shape	d [μm]	n	ϵ	Manufacturer
silica (SiO ₂)	microspheres	1.54 ± 0.02	1.37	2.8	Bangs Laboratories, Inc.
silica (SiO ₂)	microspheres	2.32 ± 0.02	1.37	2.8	Bangs Laboratories, Inc.
silica (SiO ₂)	microspheres	4.72 ± 0.04	1.37	2.8	Bangs Laboratories, Inc.
composite glass	microspheres	4.05 ± 0.03	1.52	ND	Licristar™, Merck
borosilicate glass	microspheres	9.6 ± 1.0	1.56	5.8	Duke Scientific Corp.
borosilicate glass	microspheres	20.3 ± 1.4	1.56	5.8	Duke Scientific Corp.
compound glass	microrods	1.49 ± 0.07	1.56	6.7	Nippon Electric Glass

Table 3.3: List of colloidal particles, their shape, diameter d , optical refractive index n , static dielectric constant ϵ and manufacturing company. Adapted from technical documentation of manufacturers.

In order to directly observe and control the movement of individual particles in liquid crystal host with an optical microscope, we have selected various dielectric colloidal particles with diameters ranging from 1 μm to 20 μm. These particles are mostly made of silica ($\rho_{\text{SiO}_2} = 1960 \text{ kg/m}^3$) and compound glass ($\rho_{\text{glass}} = 2500 \text{ kg/m}^3$); for details see Table 3.3. The distribution of the diameters of colloidal particles has been determined by imaging a large number of colloids under the optical microscope, followed by particle size analysis. In some cases a scanning electron microscopy (SEM) was employed to clarify the surface roughness and to determine the particle diameter more precisely, as shown in Fig. 3.2(b).

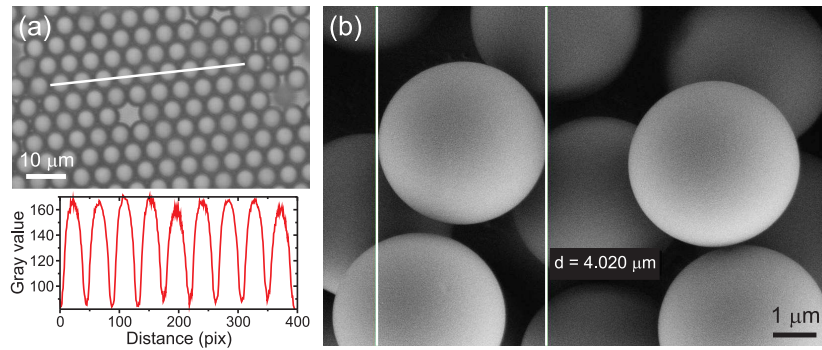


Figure 3.2: (a) Optical microscope image of 4.72 μm diameter silica microspheres with particle size analysis. (b) SEM image of 4.05 μm diameter Licristar™ spheres. Adapted from Škarabot *et al.* [96].

The surface of the colloids has been coated with a monolayer of N,N-dimethyl-N-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP silane, ABCR GmbH), which renders glass surface to low energy (e.g. turning it hydrophobic) and is known to induce very strong homeotropic liquid crystal alignment at the interface [186,187]. Dry colloidal particles have been first put into 2 wt% water solution of DMOAP. After several minutes, the dispersion was centrifuged for 30 s at 3000 rpm to force the sedimentation of particles, after which DMOAP solution was decanted and particles were rinsed with pure deionized water for several times. The purified dispersion was dried at 110 °C for 40 min to remove residual solvent. Such DMOAP-coated colloids were suspended in the nematic phase of 5CB at a typical concentration of 0.01 – 1 wt%. Finally, the mixture was subjected to sonication in an ultrasonic bath to obtain a homogeneous dispersion at room temperature.

3.1.2 Substrates and liquid crystal cell preparation

Various substrates have been used in experiments. BK7 flat glass obtained from Donnelly (USA, PD5005/5008) has been used as a basic substrate. Its static dielectric permittivity and refractive index at ambient temperature and wavelength of light $\lambda = 532$ nm correspond to $\epsilon = 6$ and $n = 1.5195$, respectively. The slides were cut into desired dimension using the glass cutter. Unless specified, 12×10 mm² slides of thickness 0.7 mm were used. Systematic procedure for the cleaning of substrates has been followed. All the glass substrates, including microscope slides and cover glasses, have been first cleaned in ultrasonic detergent bath with 10 wt% water solution of Čistko (Atotech, Slovenia) for 30 min. After cleaning in detergent, everything has been rinsed with deionized water for 5 min and finally blown with the stream of dry N₂.

After the cleaning procedure, the substrates have been subjected to various specific treatments, depending on particular experimental requirements. In order to induce homeotropic anchoring of liquid crystal molecules on the substrate, the slide and cover glass underwent the procedure of silanation. They were dipped in a 1 wt% solution of DMOAP silane in water for 10 min and then rinsed under running deionized water for several minutes to remove excess silane. Fresh DMOAP solution has been used each time the experiment was performed. At last, the substrates have been rinsed with *iso*-propanol and dried at 120 °C for 45 min. To avoid any additional contamination, all substrates were prepared immediately before the experiment.

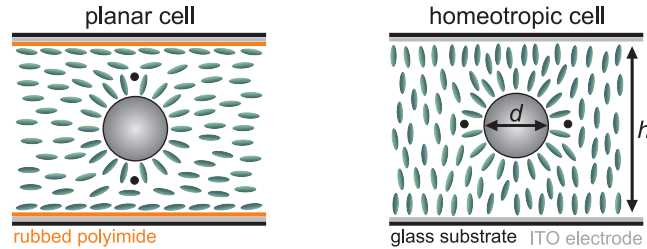


Figure 3.3: Side view of an experimental cell of thickness h and spheres with diameter d . Director field around a sphere inducing homeotropic anchoring in planar and homeotropic cell is shown schematically.

When a patterned electric field has to be applied, the transparent indium tin oxide (ITO) electrodes had to be etched on the glass substrates, before any other treatment. Firstly, the ITO glass was cut into a desired size determined by the photomask. The glass substrates were then cleaned in an ultrasonic bath and thoroughly rinsed with deionized water and *iso*-propanol. After drying in an oven at 80 °C for 20 min, the substrates were spin-coated at 4500 rpm for 30 s with a photoresist and baked on a hot plate at 80 °C for 15 min. Secondly, the substrates were exposed to UV light (Tamarack Scientific, $\lambda \approx 300$ nm, $P = 100$ mW/cm²) underneath a photomask for 10 s. After the UV exposure, the substrates were immersed in a stripper solution and the exposed photoresist was washed out. Then the substrates were treated with an acidic solution and the uncovered ITO was etched away. Finally, the patterned substrates were

sequentially rinsed with deionized water, acetone, deionized water, methanol, deionized water, *iso*-propanol to remove the residual photoresist and acid, followed by drying in the oven.

In order to achieve a planar anchoring of liquid crystal on the surfaces, the substrates were spin-coated at 3000 rpm for 30 s with a polyamic acid solution of PI-2555 (Nissan Chemicals) or PI-5291 (Brewer Science) to produce a 100 nm thick layer. The coated substrates were soft baked at 80 °C for 45 min to evaporate the solvent. Afterwards, they were hard baked at 250 °C for PI-2555 or at 230 °C for PI-5291 for 90 min to finalize the imidization reaction and consequently to form the polyimide. The surface was finally rubbed 5 times with a velvet cloth, obtaining a homogeneous planar alignment.

Samples were prepared by sandwiching a droplet of the mixture of liquid crystal and colloidal particles between two polyimide-covered (planar cell) or DMOAP-covered (homeotropic cell) ITO glass substrates, as shown schematically in Fig. 3.3. The cell gap was set between 2 μm and 20 μm , typically 20 – 80 % larger than particle diameter by using mylar spacers (5 – 12 μm thick PET films) or 2 – 5 μm big silica spheres, which ensured the unimpeded motion of the particles. In some experiments, we have also prepared wedge-type cells with thickness varying from 1 μm to 10 μm along the direction of rubbing. Before filling, the cell was sealed with a two component epoxy glue (UHU, GmbH or Torr Seal, Varian) to prevent the flow and avoid further contamination of water vapor, oxygen and organic solvents. The cell thickness was measured using spectrophotometer (USB2000+, Ocean Optics) by a standard interference technique before the nematic dispersion was filled in by capillary flow. In some cases, before filled in, the liquid crystal was heated into isotropic phase and cooled down in the vacuum to remove dissolved gas.

3.2 Polarizing optical microscopy

Optical microscopy accomplishes three tasks: *(i)* produces a magnified image of the specimen (magnification), *(ii)* separates the details in the image (resolution) and *(iii)* renders the details visible to the eye, camera, or other imaging device (contrast). The optical properties of liquid crystal phases often directly reflect the symmetry of their structures. Birefringence, that is anisotropy of the refractive index, is one of the characteristic physical properties of liquid crystals and allows for the visualization of the macroscopic molecular orientation. In thin liquid crystal cells placed between two crossed polarizers under an optical microscope, various textures, defects and interference colors can be observed, as shown in Fig. 3.4.

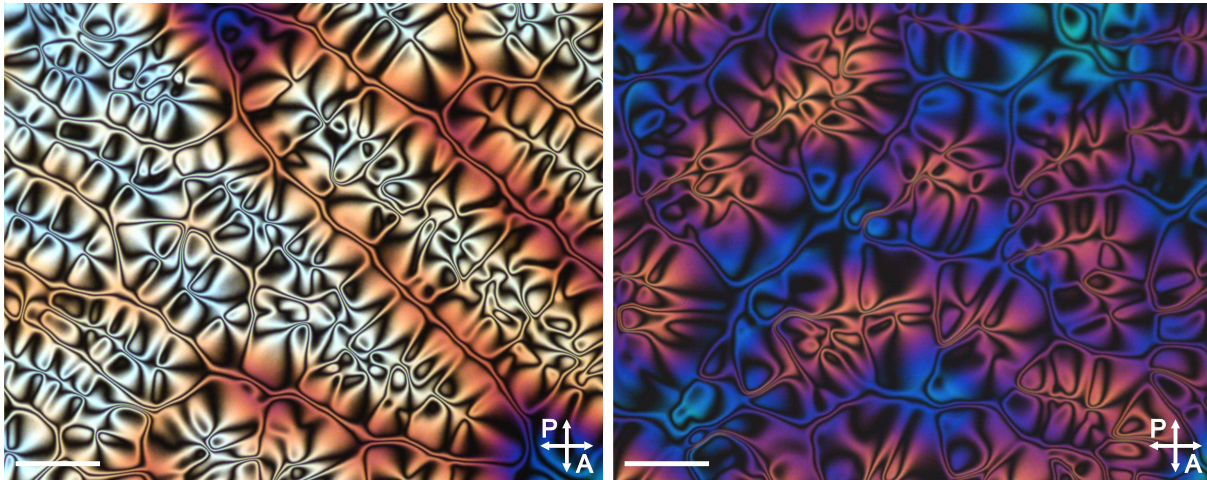


Figure 3.4: Nematic liquid crystal textures on glycerin surface viewed between crossed polarizers. Interference colors change with thickness, boundary conditions, flow and temperature. Scale bars correspond to 100 μm .

These textures and colors not only appear beautiful but also involve an information about different orientation of the optical axis in different regions of the sample. Although there are many experimental techniques to investigate the structure and physical properties of liquid crystalline phases, microscope observations often provide enough information to determine the structure even if a well-aligned domain would not be obtained. Furthermore, by applying an external field, one changes the director configuration and, consequently, the related optical properties. It is therefore of great importance to gain some background on the basic principles of light propagation in anisotropic media. This is the topic of the present Section.

3.2.1 Light propagation in anisotropic media

Any molecule, except the one with perfectly spherical shape, exhibits anisotropy in its molecular polarizability. This means that, the induced dipole moment on the molecule is the largest (or the smallest) when the external field is parallel (or perpendicular) to the axis of the largest molecular polarizability. Microscopic molecular polarizability is reflected into bulk dielectric constant $\underline{\epsilon}$. Hence, a material in which molecules have orientational ordering exhibits different dielectric constant, depending on the direction with respect to the averaged molecular orientation direction (dielectric anisotropy) and the dielectric constant is a tensor.

The propagation of light in a homogeneous medium without magnetization is described by *Maxwell's equations*, which in the absence of currents and charges write as [104]:

$$\nabla \cdot \mathbf{D} = 0, \quad \nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}, \quad (3.1)$$

where $\mathbf{D}$ is electric flux density, defined as $\mathbf{D} = \epsilon_0 \underline{\epsilon} \mathbf{E}$, and $\mathbf{B}$ is magnetic flux density, defined with magnetic field intensity $\mathbf{H} = \frac{\mathbf{B}}{\mu_0}$. In general, $\underline{\epsilon}$ is given as a second rank tensor because both $\mathbf{D}$ and $\mathbf{E}$ are three-dimensional (3D) vectors, while ϵ_0 is the vacuum permittivity and μ_0 is the vacuum permeability, respectively. In non-absorbing media, all components of dielectric permittivities are real and frequency dependent. Their values at optical frequencies ($\omega_o \sim 10^{15}$ Hz) are often substantially smaller than the static or low frequency ($\omega_s \sim 10^3$ Hz) values, especially when the material is composed of polar molecules; e.g. in water, the static permittivity is $\epsilon_s \approx 78$, but at optical frequencies, $\epsilon_o = 1.78$.

Consider a planar monochromatic wave $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$, where $\mathbf{r}$ is the position vector, directed from the source of the wave to the observation point, and $\mathbf{k}$ is the wave vector, which is real, $|\mathbf{k}| = \frac{2\pi}{\lambda} = \frac{\omega}{v}$, because the dielectric media are transparent. Finally, λ is the wavelength and v is the phase velocity of the wave. The Maxwell's equations then simplify to:

$$\mathbf{k} \cdot \mathbf{D} = 0, \quad \mathbf{k} \cdot \mathbf{H} = 0, \quad \mathbf{k} \times \mathbf{E} = \omega \mathbf{B}, \quad -\mathbf{k} \times \mathbf{H} = \omega \mathbf{D}. \quad (3.2)$$

The last set of equations implies that $\mathbf{k}$, $\mathbf{D}$ and $\mathbf{H}$ are mutually perpendicular and $\mathbf{H} \perp \mathbf{E}$. Because $\mathbf{H}$ is normal to three vectors, namely $\mathbf{k}$, $\mathbf{D}$ and $\mathbf{E}$, these three form a plane. The energy transfer vector is defined by the *Poynting vector* $\mathbf{S} = \mathbf{E} \times \mathbf{H}$. Therefore, $\mathbf{S}$ and $\mathbf{k}$ generally have different directions in an anisotropic medium. Eliminating $\mathbf{H}$ from Eq. (3.2), one obtains:

$$\mu_0 \omega^2 \mathbf{D} = k^2 \mathbf{E} - \mathbf{k}(\mathbf{E} \mathbf{k}). \quad (3.3)$$

This expression must be compatible with the constitutive equation $D_i = \epsilon_0 \epsilon_{ij} E_j$, where ϵ_{ij} are the components of the dielectric permittivity tensor $\underline{\epsilon}$. Hence follows:

$$(N^2 \delta_{ij} - N_i N_j - \epsilon_{ij}) E_j = 0, \quad (3.4)$$

where a refractive index vector $\mathbf{N} = \frac{\mathbf{k}}{\omega} \frac{1}{\sqrt{\epsilon_0 \mu_0}}$, oriented along $\mathbf{k}$, is introduced. The absolute value N is called the *refractive index* of a given wave in a given medium. Because $|\mathbf{k}| = \frac{\omega}{v}$ and $\frac{1}{\sqrt{\epsilon_0 \mu_0}}$ is the speed of light c_0 in vacuum, then $N = \frac{c_0}{v}$. The three homogeneous Eqs. (3.4) have a

non-trivial solution in $\mathbf{N}$ only if their discriminant equals to zero. This requirement results in the famous *Fresnel equation*, which reads as [104]:

$$\begin{aligned} \det(\mathbf{k}, \omega) = & N^2(\epsilon_x N_x^2 + \epsilon_y N_y^2 + \epsilon_z N_z^2) - [\epsilon_x N_x^2(\epsilon_y + \epsilon_z) \\ & + \epsilon_y N_y^2(\epsilon_x + \epsilon_z) + \epsilon_z N_z^2(\epsilon_x + \epsilon_y)] + \epsilon_x \epsilon_y \epsilon_z = 0 \end{aligned} \quad (3.5)$$

in the coordinate system with diagonalized $\underline{\epsilon}$. In uniaxial medium, where $\underline{\epsilon}$ contains only two independent entries, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$,

$$\det(\mathbf{k}, \omega) = (N^2 - \epsilon_{\perp})(\epsilon_{\parallel} N_z^2 + \epsilon_{\perp}(N_x^2 + N_y^2) - \epsilon_{\parallel} \epsilon_{\perp}) = 0. \quad (3.6)$$

Equation (3.6) shows that the surface of refractive indices Σ splits into a sphere of radius $N^2 = \epsilon_{\perp}$ and an ellipsoid of revolution $\frac{N_z^2}{\epsilon_{\perp}} + \frac{N_x^2 + N_y^2}{\epsilon_{\parallel}} = 1$, as presented in Fig. 3.5. There are two points where the two surfaces touch each other, while the axis that connects these two points corresponds to the *optical axis* of the uniaxial nematic [104]. There are two waves propagating in such a medium: the so-called *ordinary* o-wave, for which the medium behaves as an isotropic one with the index of refraction $n_o = \sqrt{\epsilon_{\perp}}$ and *extraordinary* e-wave with an index of refraction N that depends on the direction of propagation. Introducing an angle θ between the optical axis and the wave vector $\mathbf{k}$, $N_z^2 = N^2 \cos^2 \theta$, $N_x^2 + N_y^2 = N^2 \sin^2 \theta$, one gets the effective refractive index for the extraordinary wave as a function of the ray direction θ :

$$\frac{1}{N^2(\theta)} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_e^2}, \quad \text{or} \quad N(\theta) = \frac{n_o n_e}{\sqrt{n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta}}, \quad (3.7)$$

where $n_e = \sqrt{\epsilon_{\parallel}}$ is the extraordinary refractive index.

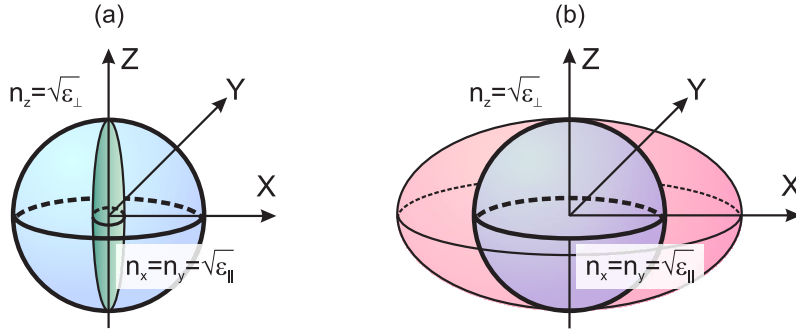


Figure 3.5: Surfaces of refractive indices for (a) an optically negative and (b) an optically positive uniaxial crystal. Adapted from Ref. [104].

The media is optically positive if $n_e > n_o$ (usually composed of elongated molecules) and optically negative if $n_e < n_o$ (usually composed of disc-like molecules) [104]. If propagation is along the optical axis, then both ordinary and extraordinary waves have the same velocity and are indistinguishable. The refractive indices n_o and n_e are inversely proportional to the phase velocity v of the propagating wave, leading to $n_o = \frac{c_0}{v_o}$ and $n_e = \frac{c_0}{v_e}$. Difference in velocity between two waves results in the phase shift (retardation), which is given by

$$\Delta\varphi = \frac{2\pi}{\lambda_0}(n_e - n_o)h, \quad (3.8)$$

where h is thickness of the sample, $n_e - n_o = \Delta n$ is birefringence and λ_0 is the vacuum wavelength of light. A typical birefringence of 5CB liquid crystal material is 0.2.

3.2.2 Polarized light in nematic liquid crystal

The rule that the plane of polarization of the e-wave always contains a component along the director $\mathbf{n}$, whereas the o-wave is always polarized normally to $\mathbf{n}$, proves useful in observations with polarized light. Considering nematic slab sandwiched between two glass plates and placed between two crossed polarizers [see Fig. 3.6(a)], one can introduce the in-plane dependence of director orientation $\mathbf{n}(x, y)$. The light beam impinges normally to the cell, that is along the z axis. A polarizer placed between the source of light and the sample makes the impinging light linearly polarized. In the nematic, the linearly polarized wave of amplitude A and intensity $I_0 = A^2$ splits into the ordinary and extraordinary waves with mutually perpendicular polarizations and amplitudes $A \sin \beta$ and $A \cos \beta$, respectively, where $\beta(x, y)$ is the angle between the local $\mathbf{n}(x, y)$ and the polarization of incident light. The vibrations of the electric vectors at the point of entry are in phase. However, the two waves take different times, $n_o \frac{h}{c_0}$ and $n_e \frac{h}{c_0}$, respectively, to pass through the slab. At the exit point, the electric vibrations $A \sin \beta \cos(\omega t - \frac{2\pi}{\lambda_0} n_o h)$ and $A \cos \beta \cos(\omega t - \frac{2\pi}{\lambda_0} n_e h)$ gain a phase shift $\Delta\varphi = \frac{2\pi}{\lambda_0} (n_e - n_o) h$. The projections of these two vibrations onto the polarization direction of the analyzer behind the sample are:

$$a = A \sin \beta \cos \beta \cos\left(\omega t - \frac{2\pi}{\lambda_0} n_o h\right), \quad b = -A \sin \beta \cos \beta \cos\left(\omega t - \frac{2\pi}{\lambda_0} n_e h\right). \quad (3.9)$$

When two harmonic vibrations $A_1 \cos(\omega t + \varphi_1)$ and $A_2 \cos(\omega t + \varphi_2)$ of the same frequency occur along the same directions, then the resulting vibration $\bar{A} \cos(\omega t + \bar{\varphi})$ has an amplitude defined as $\bar{A}^2 = A_1^2 + A_2^2 + 2A_1 A_2 \cos(\varphi_1 - \varphi_2)$. The analyzer, thus, transforms the pattern of (x, y) -dependent phase difference into the pattern of transmitted light intensity $I(x, y) = \bar{A}^2$. The intensity of light passed through the crossed polarizers and the nematic slab between them follows from Eq. (3.9) as

$$I = I_0 \sin^2 2\beta \sin^2 \left[\frac{\pi h}{\lambda_0} (n_e - n_o) \right]. \quad (3.10)$$

The last equation refers to the case when $\mathbf{n}$ is perpendicular to the axis z . If $\mathbf{n}$ makes a constant angle θ with the axis z , then Eq. (3.10) becomes:

$$I = I_0 \sin^2 2\beta \sin^2 \left[\frac{\pi h}{\lambda_0} \left(\frac{n_o n_e}{\sqrt{n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta}} - n_o \right) \right]. \quad (3.11)$$

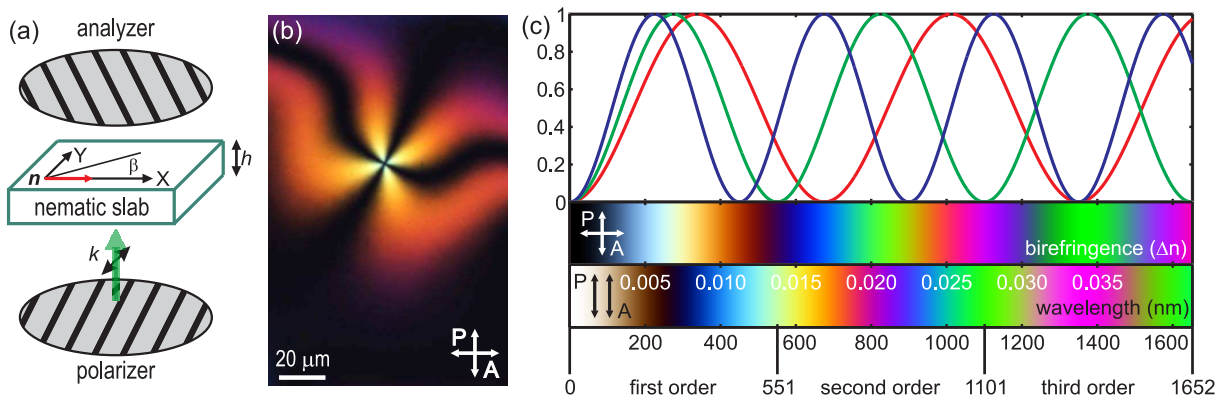


Figure 3.6: (a) Propagation of light through a polarizer, uniaxial nematic slab, and analyzer. (b) Schlieren texture of a thin film of the nematic 5CB on a glycerin substrate. Note the interference colors: dark brushes mark the regions in which the director is parallel to either the polarizer or the analyzer. Nodes in which four brushes meet are cores of topological point defects. The image is adapted from Ref. [5]. (c) A reduced Michel-Levy chart showing the colors of an optically anisotropic sample between crossed and parallel polarizers, as a function of the birefringence Δn .

Equations (3.10) and (3.11) are fundamental for understanding liquid crystal textures. Firstly, the phase shift $\Delta\varphi$ and, thus the intensity I depends on λ_0 . Consequently, the sample would show a colorful texture, when being illuminated with a white light because the maximum of transmitted light intensity depends on the angle θ . The interference colors are especially pronounced when $(n_e - n_o)h \approx 3\lambda_0$. With typical $(n_e - n_o) \approx 0.2$, $\lambda_0 \approx 500$ nm, the colorful range of thicknesses is $h \sim 10$ μm . Secondly, the director tilt θ greatly changes the phase shift. In the case of homeotropic orientation ($\mathbf{n} \parallel z$, $\theta = 0$) the sample looks dark; only the ordinary wave propagates and according to Eq. (3.11), $I = 0$. Thirdly, if $\theta > 0$ but $\beta = 0, \pm\frac{\pi}{2}, \dots$, one might still observe dark brushes, even in monochromatic light, as shown in Fig. 3.7(a). In a sample with in-plane director distortions $\mathbf{n}(x, y)$, wherever $\mathbf{n}$ is parallel or perpendicular to the polarizer, the propagating mode is either pure extraordinary or pure ordinary and the corresponding region of the texture appears dark again. Figures 3.6(b) and 3.7(a) show examples of such textures with dark brushes. Points at which the brushes converge are centers of topological defects and such a texture is called the *Schlieren texture*.

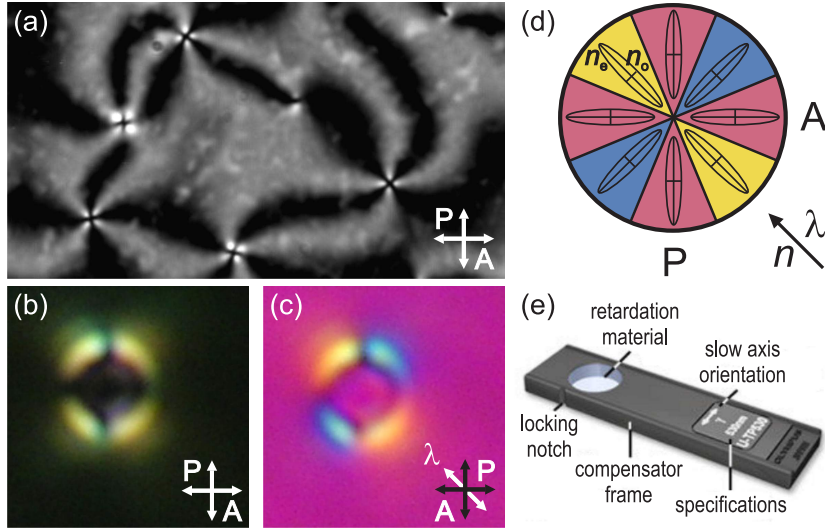


Figure 3.7: Photomicrographs of the 5CB nematic liquid crystal taken between crossed polarizers. (a) Schlieren texture in a 10 μm thick planar cell. ± 1 point defects and $\pm \frac{1}{2}$ disclination lines can be observed. (b) Homeotropic colloid in a homeotropic cell as observed between crossed polarizers without and (c) with inserted optical compensator. (d) Relation between the orientation of the liquid crystal molecules and the color, observed under the polarizing optical microscope, when the red plate λ is inserted at 45° with respect to polarizer P and crossed analyzer A. (e) Example of the red plate optical compensator.

In principle, by rotation of crossed polarizers, one can reconstruct the whole in-plane director pattern of the Schlieren texture. However, there is an ambiguity: since $I \propto \sin^2 2\beta$, the reconstruction produces two director patterns, $\beta(x, y)$ and $\beta(x, y) + \frac{\pi}{2}$. To map the in-plane director configuration unambiguously, one has to use optical compensators or quartz wedges. Compensators are plates with a known phase shift. For our experiments we have used red plate, which provides a phase shift equal to 530 nm. The plate has two well-defined directions, with a minimum refractive index n_{min} , referred to as 'fast axis', and n_{max} , called the 'slow axis'. The compensator is inserted into the slot between the sample and the analyzer at 45° with respect to the polarizer and analyzer directions. The black brushes of the texture become red because the sample's phase retardation in these regions is zero and the total phase retardation is defined entirely by the compensator, as shown in Fig. 3.7(b, c). The region where the director is parallel to the fast direction and the region where the director is parallel to the slow direction would acquire different interference colors and, thus, can be distinguished. Without the compensator, these regions would be equally bright because for both of them $I \propto \sin^2 2\beta = \sin^2 \frac{\pi}{2} = 1$ in Eq. (3.11). Nevertheless, the measurements of the transmitted light intensity has been used to

monitor the switching of molecular orientation in the Fréedericksz transition [188] to measure the temperature dependence of Frank elastic constants and to measure the anchoring strength [109].

All the optical observations have been performed through (de)polarized transmitted light microscopy with a Nikon Eclipse E600 polarizing optical microscope, in particular cases as a function of liquid crystal cell temperature, controlled by Instec STC200D heating stage and under the influence of external electric field, generated by programmable function generator Hameg HM8130. Red plate $\lambda = 530$ nm and orthogonal Nikon polarizers were used to acquire color images by Nikon Coolpix E5400 digital camera, while other images and videos were captured by monochromatic PixeLINK PL-A741 camera. Image analysis was performed with Adobe Photoshop, Corel Draw, ImageJ, IrfanView, Origin and Matlab software.

3.3 Optical tweezers

Optical tweezers, also called laser tweezers, are a scientific instrument that uses highly focused laser beam to trap, manipulate and measure forces on microscopic dielectric objects. The investigation of optical tweezing has started in early 1970s by Arthur Ashkin [189] with the first observation of acceleration of freely suspended latex microspheres by the forces of radiation pressure from a weakly focused laser beam. The objects were confined on the optical axis and propelled in the direction of light propagation. Soon afterwards, Ashkin was able to guide the particles with a refractive index higher than the surrounding medium in a liquid or air environment and even trap them in an inverted geometry where the laser light pressure was balanced by the gravitation force [190–192].

The single beam gradient optical tweezers that enable 3D trapping of particles were developed by Ashkin, Steven Chu and coworkers in 1986 [193]. Since then there has been continuous development of the technique with many new applications. The technique has matured and today optical tweezers are highly effective research tool used in various fields (for an extensive review see [194–198]). They are particularly important in biophysics and biology by providing a non-contact and non-invasive way of manipulating cells, organelles and particles at sub-micrometer precision and to measure forces in the range of 0.1 – 100 pN [199–204].

3.3.1 Basic theory of optical trapping

An optical trap is created by focusing a laser beam to a diffraction-limited spot using a high numerical aperture objective. Strong gradient of light intensity near the focus creates a 3D potential well for particles with a refractive index higher than that of the surrounding medium. If there is no difference in the refractive index of the particle and its surroundings, there is no optical force exerted on the particle. If the refractive index of the particle is lower than that of the medium, the particle is expelled from the beam center.

In the ray optics regime, where a particle is much larger than the wavelength of light used for trapping, the optical force on a particle in a tightly focused laser beam can be decomposed into two components: a scattering component (radiation pressure), which acts in the direction of the beam propagation, and a gradient component (which arises from induced dipole interactions with the electric field gradient) in the direction of highest light intensity. Figure 3.8 qualitatively depicts the origin of the optical force and explains how momentum (each photon is carrying a linear momentum determined by the wavelength of light $p = \frac{E}{c} = \frac{h}{\lambda}$) changes of p_1 and p_2 rays differ in magnitude, causing a lateral gradient component. The axial gradient component is also caused by momentum transfer upon refraction, resulting in a restoring force towards the focus, as can be seen in Fig. 3.8(b, c). The figures do not take into account the fact that part of the incoming light is reflected rather than refracted (the scattering component). The particle is stably trapped at the point where the gradient component, the scattering component and the gravitational force balance.

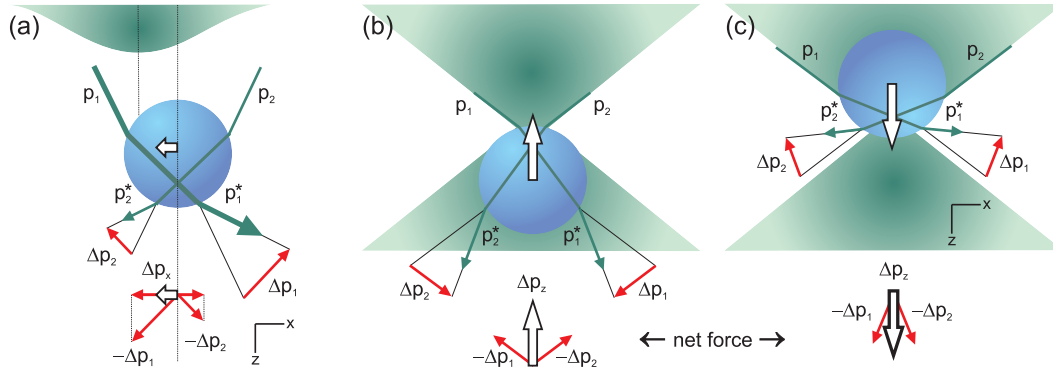


Figure 3.8: Qualitative picture of the optical force origin. Image (a) shows the lateral gradient force of a Gaussian laser beam. Images (b) and (c) show the axial gradient force towards the focus of the trapping light. Since rays momentums p_1 and p_2 come from parts of the beam with different intensity, the momentum changes Δp_1 and Δp_2 differ in magnitude, causing a net restoring force, indicated by white arrows. The scattering component that tends to expel the object from the focus is not shown. Adapted from Ref. [205].

The optical force acting on a spherical particle can be analytically calculated in ray optics regime by using Fresnel equations for reflection and transmission coefficients R and T [206]. The scattering component can be expressed as

$$\mathbf{F}_{scatt} = \frac{n_1 P}{c_0} \left[1 + R \cos 2\theta - T^2 \frac{\cos(2\theta - 2\phi) + R \cos 2\theta}{1 + R^2 + 2R \cos 2\phi} \right] = \frac{n_1 P}{c_0} Q_{scatt}, \quad (3.12)$$

where n_1 is refractive index of the surrounding medium, θ and ϕ the angles of incidence and refraction, and c_0 the speed of light. The angles θ and ϕ are related via Snell's law $\frac{n_2}{n_1} = \frac{\sin \theta}{\sin \phi}$, where n_2 is the refractive index of the particle. Similarly, the gradient component equals

$$\mathbf{F}_{grad} = \frac{n_1 P}{c_0} \left[R \sin 2\theta - T^2 \frac{\sin(2\theta - 2\phi) + R \sin 2\theta}{1 + R^2 + 2R \cos 2\phi} \right] = \frac{n_1 P}{c_0} Q_{grad}. \quad (3.13)$$

Vectorial addition of these two optical force components gives for the magnitude of the force due to a single ray of power P :

$$F = \frac{n_1 P}{c_0} \sqrt{Q_{scatt}^2 + Q_{grad}^2} = \frac{n_1 P}{c_0} Q(\theta, \frac{n_2}{n_1}, R, T), \quad (3.14)$$

where the variables determining the effective Q -value have been explicitly stated. The total force on the object is found by summing over all rays passing through it.

If the diameter of the particle is much smaller than the wavelength of the trapping light, we refer to Rayleigh regime. Then, a spherical particle of refractive index n_2 embedded in a medium of refractive index n_1 in the proximity of a focused Gaussian beam experiences a potential [205]:

$$U = -\frac{3Vn_1}{c_0} \left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \right] I_0 \exp\left(-\frac{r^2}{w_0^2}\right), \quad (3.15)$$

where V is the volume of the particle, I_0 is the laser intensity and w_0 is beam waist diameter at the focus. The optical force on the particle as it moves from the equilibrium position $r = 0$ is

$$\mathbf{F} = -\nabla U = \frac{6Vn_1}{c_0 w_0^2} \left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \right] I_0 \exp\left(-\frac{r^2}{w_0^2}\right) r\mathbf{r}. \quad (3.16)$$

Therefore, for small displacements from the equilibrium position an optical trap exerts an elastic force $F_i = k_i r_i$ ($i = x, y, z$), with k_i being the stiffness of the trap along a given direction. Normal optical traps are produced by a tightly focused laser beam with a Gaussian profile, often referred to as TEM₀₀ mode, where radial forces are larger than the axial one ($k_x = k_y > k_z$).

However, neither the ray optics nor the Rayleigh approach is quantitatively applicable to practical applications in our experiments, since the particle size and the wavelength of the trapping light are often comparable, that is in Mie regime [206]. The calculation of optical force on a trapped particle in this regime is complex and has to be performed numerically. Fortunately, for most applications of optical tweezers there is no need for force calculation because the tweezers are experimentally characterized and calibrated before they are used for quantitative measurements.

3.3.2 Force calibration

There are several methods enabling the calibration of optical tweezers, however, the same basic principle is used by all of them. In order to measure the force acting on a particle within an optical trap, one has to know the displacement of the particle from the equilibrium position and the stiffness of the trap. There are numerous possibilities to measure the trap stiffness and perhaps most popular is stiffness calibration from the power spectral density of the trapped particle's fluctuations or the use of the equipartition theorem.

A trapped particle undergoes a confined Brownian motion. If the particle is embedded in a Newtonian fluid (a fluid whose stress is linearly proportional to strain rate - the constant of the proportionality is the viscosity), the displacements from the equilibrium position $[x(t), y(t), z(t)]$ can be described by the Langevin equation [122], which for one dimension reads as

$$m \frac{d^2 x}{dt^2} = -\gamma \frac{dx}{dt} - kx + F(t), \quad (3.17)$$

where m is the mass, k is the trap stiffness and $\gamma = 6\pi\eta r$ is the viscous drag coefficient of the particle. Micrometer-sized particles moving with a typical velocity $\mu\text{m/s}$ have low Reynolds number, therefore the inertial term in Eq. (3.17) can be neglected. $F(t)$ represents the random thermal force, which averages to zero over time. The power spectrum of $F(t)$, $S_F(t)$, contains the contribution of motions with different frequencies. For idealized Brownian motion this corresponds to white noise, therefore the power spectrum is a constant [122]:

$$S_F(t) = |\mathcal{F}(f)|^2 = 4\gamma k_B T, \quad (3.18)$$

where $\mathcal{F}(t)$ is the Fourier transform of $F(t)$. After calculating the Fourier transform of the Langevin equation (3.17), writing $\mathcal{X}(f)$ as the Fourier transform for $x(t)$, and taking the modulus on both sides, the power spectrum of the displacement fluctuations is found to have a Lorentzian shape [122]:

$$S_x(f) = |\mathcal{X}(f)|^2 = \frac{k_B T}{\gamma \pi^2 (\nu_c^2 + \nu^2)}, \quad (3.19)$$

where corner frequency $\nu_c = \frac{k}{2\pi\gamma}$ is directly related to trap stiffness k . At low frequencies $\nu \ll \nu_c$, the power spectrum is roughly constant

$$S_0 = |\mathcal{X}(0)|^2 = \frac{4\gamma k_B T}{k^2} \quad (3.20)$$

and it contains information on the confinement of the particle as well. A typical power spectrum is shown in Fig. 3.9(a).

The fastest way to calibrate the trap stiffness k of the trapped particle is by the use of the equipartition theorem [122]:

$$\frac{1}{2} k_B T = \frac{1}{2} k \langle x^2 \rangle. \quad (3.21)$$

By measuring the average squared displacement $\langle x^2 \rangle$ of the fluctuations of the trapped particle, the trap stiffness $k = k_B T / \langle x^2 \rangle$ is easily obtained.

The trap stiffness is typically linearly dependent on the power of the incident laser beam. This is demonstrated in Fig. 3.9(b), where the stiffness k as a function of laser power for $1.0 \mu\text{m}$ diameter silica particle, trapped in water, is presented.

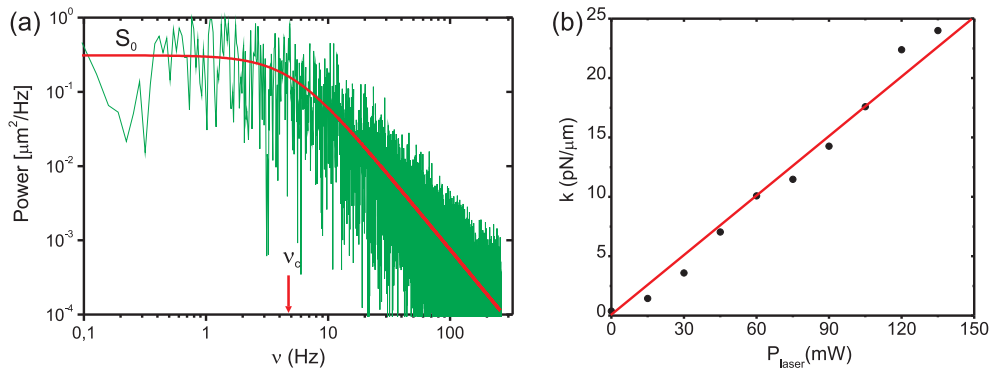


Figure 3.9: Calibration of optical trap stiffness. (a) Typical power spectral density of a trapped particle in water. Red curve is fit to (3.19) with $\nu_c = 4.92$ Hz. (b) Trap stiffness k for $1 \mu\text{m}$ big silica particle in water as a function of laser power. Adapted with permission from Osterman *et al.* [144].

3.3.3 Experimental setup

A basic version of optical tweezers setup consists of a laser source and an objective with high numerical aperture, which creates one stationary optical trap. Since such design is quite limiting for experimental work, the setup usually includes a system for laser beam steering. There are many possibilities for a beam steering, starting from simple manual mirrors, piezo-driven mirrors and more complex techniques such as spatial light modulators or acousto-optic deflectors. A laser is chosen according to the optical tweezers application. Typically, high power, single mode laser with a good pointing stability and low power fluctuations is desired. Most optical tweezers are built around modified, commercially available microscopes, which are simultaneously used to image the sample. Inverted microscopes are more convenient because gravitational force on a trapped particle counteracts the scattering force, thus, better trapping is achieved in three dimensions. The laser beam is fed into the objective using a dichroic mirror, which reflects the trapping laser beam and transmits the light used for imaging. Samples are imaged by CCD or CMOS camera.

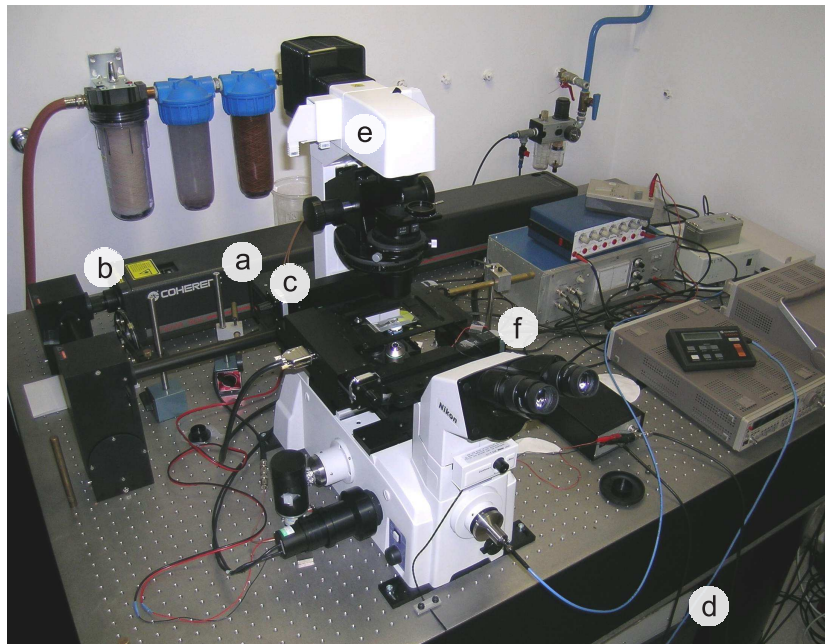


Figure 3.10: Experimental setup in our laboratory: (a) Ar+ ion laser, (b) laser output, (c) box with acousto-optic deflectors, (d) beam steering controller, (e) inverted microscope, (f) CMOS camera.

Our optical tweezers setup (LTM-N2000-A, Aresis) was built around inverted optical microscope (Nikon Eclipse TE2000-U), equipped with motorized stage (Prior OptiScan II), halogen lamp and ion laser source. The laser beam is spatially controlled with a pair of acousto-optic deflectors (AA Opto-electronic, DTSXY-400-532, frequency range of acoustic waves from 115 – 160 MHz), driven by a beam steering controller (Aresis, BSC-01), which enables creation of multiple optical traps and their precise positioning. A custom software (Aresis, Tweez v2.1), running on a PC, connected with the beam steering controller and fast CMOS camera (PixeLINK, PL-A741, 1280x960 pixels, physical pixel size $6.7 \mu\text{m}$), is used to manipulate traps and to record experimental videos. Maximum frame rate of the camera is 25 frames per second (fps) for full frame images, whereas smaller regions of interest (ROI) can be recorded with higher frame rates, inversely proportional to the size of ROI, i.e. maximum frame for ROI of 256×256 pixels is 450 fps. The camera can be synchronized to optical tweezers using a beam steering controller as an external trigger. The photograph and schematics of experimental setup are shown in Fig. 3.10 and Fig. 3.11, respectively.

The laser source is Ar⁺ ion laser (Coherent, Innova 90C-4) with wavelength of 514.5 nm and 1.7 W of maximum power. It outputs linearly polarized Gaussian beam in TEM₀₀ mode. The laser beam is expanded to match the entrance pupil of the acousto-optic deflectors (AODs), which are used to deflect the beam and therefore change its position in the sample. A telescope optics and three mirrors are used to align the beam from the AODs to the entrance pupil of a high numerical aperture water immersion microscope objective (Nikon NIR Apo 60x/1.0w). Optical elements in the beam path gradually reduce the beam power. Transmission ratio from the laser source through AODs, telescope optics and microscope tube lens corresponds to approximately 30 %, transmission of the objective is 50 %, giving the total transmission of 15 % from the laser to the sample. In experiments where AOD field flattening was used the total transmission was additionally reduced to overall 10 %.

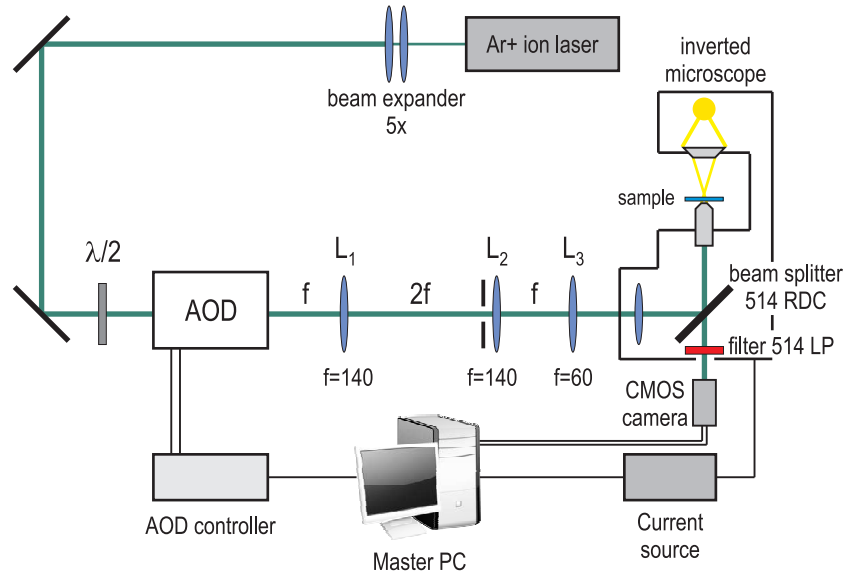


Figure 3.11: Schematics of the optical tweezers setup. Laser beam is expanded and guided through a pair of orthogonal acousto-optic deflectors to the entrance pupil of the microscope objective. Master PC controls the beam steering controller, a CMOS camera and motorized stage mounted on the inverted microscope.

The AOD diffraction angle depends on the frequency of acoustic wave inside the AOD. Since the beam steering controller creates it by direct digital synthesis with relative frequency resolution 10^{-9} , the trap position can be changed in sub-nanometer steps. Trap stiffness is controlled by varying AOD transmission, which depends on the acoustic wave amplitude. Multiple traps can be created by time sharing of the laser beam. The beam steering controller supports up to a

few thousands individual quasi-simultaneous traps or hundred thousands traps in a sequence. A pair of acoustic waves that define the trap position and stiffness can be switched to different pair with user defined rate between 100 Hz and 100 kHz, which is needed for time sharing of the beam due to a creation of multiple traps. When the AOD switching rate is high, a particle, trapped in one of N simultaneous traps, 'feels' as it is trapped in a single trap with roughly N times lower stiffness. For instance, if switching rate is 100 kHz and there are 10 simultaneous traps, each trap gets a laser pulse, 10^{-5} s long every $9 \cdot 10^{-5}$ s. Since the self-diffusion time $\tau = \frac{3\pi\eta}{2k_B T} r^3 \approx 1.15$ s for particle in water with radius $r = 1 \mu\text{m}$ is much longer than that [122], the particle is in a quasi-stationary trapping potential. On the other hand, lower AOD switching rate enables precise control over the movement of individual traps. For example, if the switching rate is 1000 Hz and there are 1000 traps, sequently arranged in a circle, the particle feels a single trap that is traveling around a circle with frequency 1 Hz. The efficiency of AODs varies with frequency of acoustic wave, which results in a trap stiffness variation, depending on its position. In order to maintain equal trap stiffness everywhere in a trapping region, AOD field flattening was used. A separate photodiode connected to the beam steering controller was used to scan the laser power across the complete trapping region. A field flattening look-up table was created and subsequently used directly in an acoustic wave generation procedure.

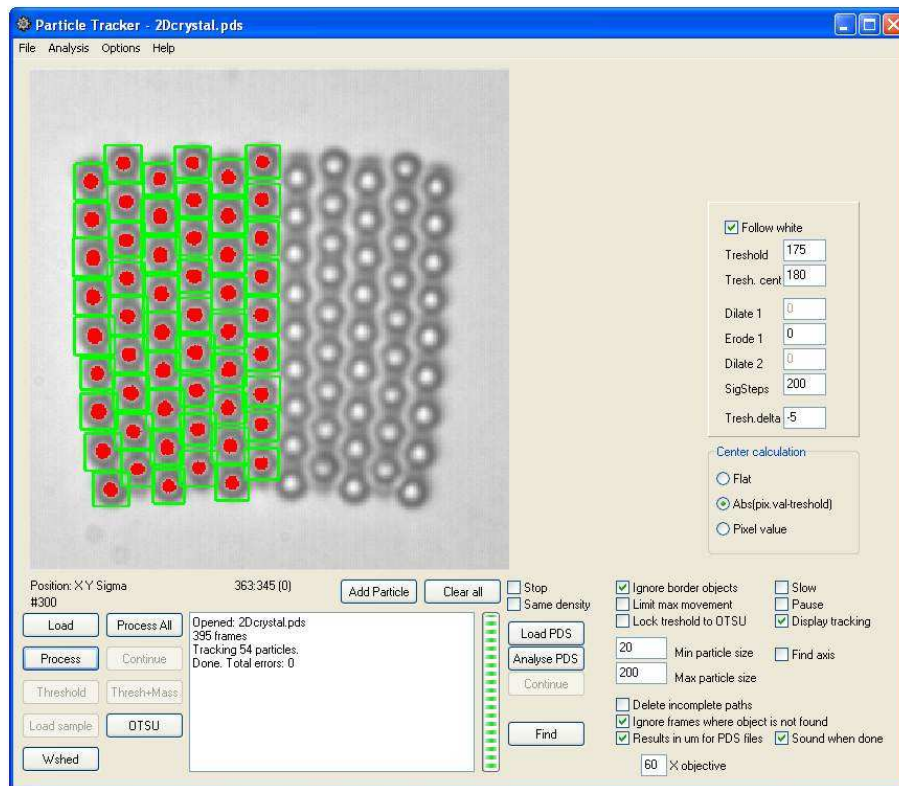


Figure 3.12: Screenshot of *PartTrack* software after successful tracking of 54 particles. Tracked particles are labeled with red, their positions through the video are written to a hard disk in a plain text format.

We have used a special camera control and acquisition module for the optical tweezers software. The raw data from the camera is recorded to a hard disk in a custom format, where each frame is accompanied by a frame header that carries frame specific information, such as exact frame time and positions of optical traps. Custom particle tracking software *PartTrack* was developed by Osterman *et al.* [144] for off-line analysis of experimental videos. Particle recognition and tracking of videos, where objects do not come into contact, are based on standard digital video microscopy tracking algorithms [207]. In more complex situations convolution techniques embedded in tracking procedures are applied [144]. Tracking accuracy depends mainly on a

particle size; larger size means better accuracy. A micrometer-sized particle is imaged to roughly 70 square pixels. Test videos of such particle, fixed to the surface of a sample cell, revealed that the position accuracy is ± 5 nm. Typically, we used even larger microspheres, therefore their positions were determined with even better accuracy. The software is able to automatically detect multiple particles in the first frame of a video according to user-defined criteria (such as particle size and shape) and then follow them in subsequent frames (see Fig. 3.12). In order to successfully create a trajectory from the array of particle positions in each frame, certain requirements have to be met, most importantly the displacements of particles from frame to frame have to be smaller than the average separation between the particles.

3.3.4 Optical trapping of colloidal particles in a nematic liquid crystal

In recent years there has been a growing interest in optical trapping inside anisotropic fluids, particularly within liquid crystals. Since first experiments performed by Muševič *et al.* [50] and Yada *et al.* [51] in 2004 anisotropic interactions between colloidal particles in nematic liquid crystal have been extensively investigated experimentally using combined optical microscopy and optical tweezers. The breakthrough results were obtained by Muševič and coworkers [50,208,209], who have reported that, contrary to intuition, colloidal particles with refractive index lower than both refractive indices of a birefringent liquid crystal can be effectively trapped into the laser focus. This finding has initiated the field of optical manipulation of colloidal particles in anisotropic fluids and has crucially facilitated the assembly of regular colloidal structures.

In the breakthrough article, Muševič *et al.* [50] have revealed two different mechanisms that are responsible for the anomalous colloidal trapping. Firstly, below the optical Fréedericksz transition, the trapping is due to the anisotropic dielectric interaction of the polarized light with the inhomogeneous director field around the colloid. The particle is therefore 'dressed' with high-index corona and behaves effectively as a high-index particle compared to surroundings. The second trapping mechanism includes optically induced distortion above Fréedericksz transition, which causes local decrease or even melting of the order parameter of a birefringent fluid [7]. This creates a 'ghost' colloid at the laser focus point that acts as a long-range trapping site, attracting the particle over several micrometers. Sequences of micrograph images in Fig. 3.13, taken between crossed polarizers, show both types of trapping mechanisms, below and above the optical Fréedericksz transition, respectively.

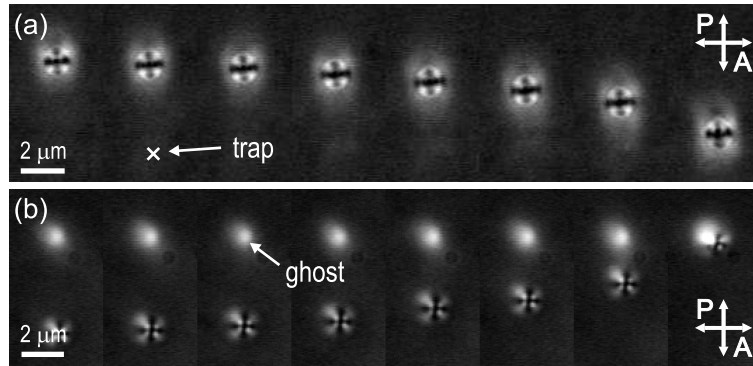


Figure 3.13: Sequences of polarized optical micrographs, showing two trapping events in 50 μm thick layer of 5CB. The time steps are equal for both images. (a) Trapping at low power of 25 mW is just below the power necessary to induce the optical Fréedericksz transition. (b) Trapping at 35 mW, which is above the optical Fréedericksz transition. The bright spot is due to a local birefringent area, created by the laser-induced distortion of the director field. Adapted with permission from Muševič *et al.* [50].

In order to get more insight into the nature of this extraordinary attraction, the strength of confinement of colloidal particle in a light trap was determined from recorded trajectory of the particle during its Brownian motion in the plane of the cell. The probability density $P(r)$ to

find a particle at a given distance r from its equilibrium position is given by [50]:

$$P(r) = Ar \exp\left(-\frac{U(r)}{k_B T}\right). \quad (3.22)$$

In the vicinity of the equilibrium point, the potential well $U(r)$ can be treated as a parabolic one, $U(r) = \frac{1}{2}kr^2$. The trap stiffness k is therefore obtained by fitting the experimentally determined probability distribution $P(r)$. Results are shown in Fig. 3.14 for laser power of 8 mW and 32 mW, respectively. Figure 3.14(a) shows the positions of a colloid in the (x, y) plane, recorded during the Brownian motion in an optical trap and the corresponding histograms for each coordinate. The probability distribution $P(r)$ is symmetric with respect to x, y coordinates and shows perfect agreement with a Gaussian fit, demonstrated in Fig. 3.14(b). Finally, the reconstructed profile of the laser trapping potential is presented in Fig. 3.14(c), together with a parabolic fit. The corresponding trap stiffness equals to 9.2 pN/ μ m for 32 mW laser power and is reduced to 2.0 pN/ μ m for 8 mW, as expected [50].

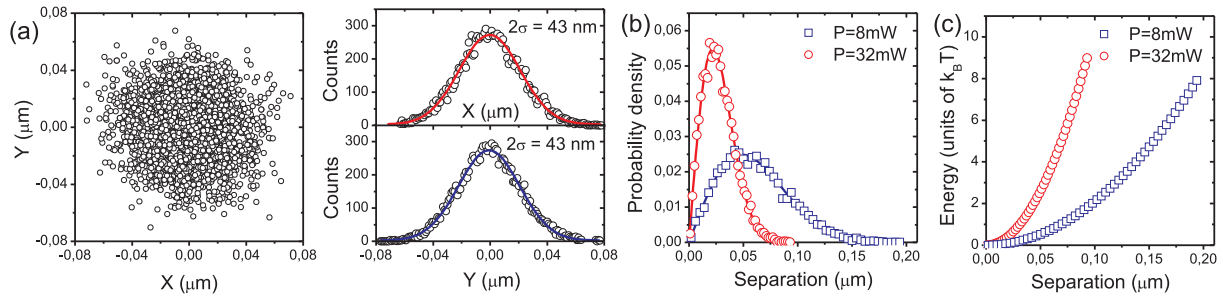


Figure 3.14: (a) The positions and corresponding histograms of 5000 points recorded during the Brownian motion of 1 μ m big silica particle in an optical trap in homeotropically aligned 5CB. (b) The probability density $P(r)$ for the Brownian cloud at two power levels and (c) the reconstructed profile of the optical potential. Adapted with permission from Mušević *et al.* [50].

Further on, it has been demonstrated that optical trapping of colloidal spheres in a nematic fluid is direction sensitive and can be controlled by changing the polarization of the laser beam [79,208,209]. The unique trapping properties arise because a linearly polarized beam propagating in the anisotropic medium 'sees' the local effective refractive index that depends on the director and the light polarization state. Optical forces are therefore varied by changing the beam polarization and particle's surface characteristics, even up to an extreme situation, when a particle is attracted at some polarizations but repelled from the beam with other polarization states [79,208,209]. The trapping forces between two elastic dipoles were measured statically by determining a threshold power of the trapping beam, which was required to keep the particles at a given separation [51,78,79,210]. These forces are nearly proportional to r^{-4} in a limited size of reduced separation, thus confirming the dipolar nature of the attractive force [51,136]. A combination of static and dynamic measurements gave the angular dependence of the force between two elastic quadrupoles [78]. Dynamic measurements, where the trajectory of the released particle was observed, were used to study the interactions between elastic dipoles and quadrupoles [33,34,80,81]. The optical tweezers were also used for switching liquid crystal droplets [211–214], optical manipulation of defects in lyotropic liquid crystals [215,216], manipulation of islands on freely suspended smectic films [217–219] and lately for production of optical vortices [220] and electrically tunable optical microresonators from liquid crystal droplets [221].

In the present work we have used optical tweezers to manipulate individual particles and to precisely measure the interactions between elastic dipoles and quadrupoles in homogeneous and chiral nematic environments. The results are extensively presented in the following Chapters.

Introduction to nematic colloidal structures

In this Chapter we present the results that have been obtained in our research group during the first two years of my postgraduate study. These achievements comprehend many important strategies and conceptual shifts that have enabled the evolution of my original contributions, presented in the following Chapter. The presented experiments have been initiated and supervised by Igor Muševič. The experimental work was performed by Miha Škarabot and some analysis were accomplished by myself. We have shown that stable two-dimensional nematic colloidal crystals can be built from elastic dipoles and quadrupoles in confined nematic layers using optical tweezers. The assembly process was studied also under applied external electric field, which enabled the massive transport and crystallization of colloidal particles. Furthermore, elastic dipole to quadrupole transition was experimentally studied along with confinement effect that influences the stability of colloidal structures. Experiments with entangled colloids were initiated by numerical simulations of Miha Ravnik and Slobodan Žumer, who predicted a new way of colloidal binding, where two particles are entangled by delocalized defect loops. The results were presented in our joint publications [31,80–83,96].

4.1 Colloidal monomers and dimers

4.1.1 Elastic dipoles and quadrupoles

When a single micrometer-sized particle with homeotropic surface anchoring is introduced into a nematic liquid crystal, two characteristic director field configurations form around the particle: either an elastic dipole or an elastic quadrupole. Which of the two possible structures is stable and which is metastable depends primarily on the particle size, surface anchoring strength, confinement and external field [21].

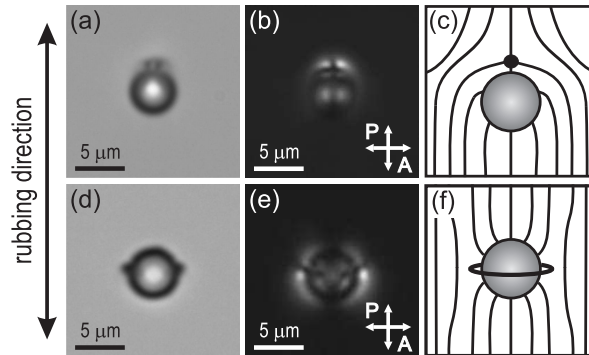


Figure 4.1: Spherical particle embedded in a nematic liquid crystal induces elastic dipole or quadrupole. (a) Optical micrograph of silica microsphere in $9\ \mu\text{m}$ thick layer of 5CB with a hyperbolic point defect. (b, c) The nematic order around the colloid, observed between crossed polarizers, has the symmetry of an electric dipole. (d-f) The nematic order around the same microsphere in $5.5\ \mu\text{m}$ thick layer of 5CB has the symmetry of an electric quadrupole with a Saturn ring encircling the particle.

Figure 4.1 shows several optical micrographs of spherical silica colloid ($r_c = 2.36 \mu\text{m}$), embedded in a thin layer of 5CB nematic liquid crystal. The structure of the director field around the particle can be observed between crossed polarizers [Fig. 4.1(b)] and afterwards schematically illustrated [Fig. 4.1(c)]. It is distorted dipolarly, with a hyperbolic point defect [19,21] that appears as a dark spot on top of the particle in Fig. 4.1(a). The colloidal particle and the point defect are oriented along the rubbing direction and they can be considered as a pair of two topological point defects carrying the opposite topological charge of magnitude 1. Such configuration is an analog of the electrostatic dipole, which here reflects the global conservation of topological charges, during the process of inserting the colloidal particle in the homogeneous nematic field [21,138,143]. For thickness smaller than the critical one, the dipolar field around the colloidal particle is strongly influenced by the confining surfaces. The symmetry of the director field around the particle becomes quadrupolar, as shown in Fig. 4.1(e, f), with a closed disclination loop, that encircles the particle and is called the Saturn ring [21,23]. Two black spots on both sides of the colloid in Fig. 4.1(d) represent the top view of the Saturn ring.

The hyperbolic point defect of the dipolar configuration readily opens into a small ring in order to minimize the free energy, which is a known result for Landau-de Gennes model [140,141]. The position of the hyperbolic defect ring, determined from the image analysis, is at $1.36r_c$, which is in reasonable agreement with results from Ravnik [222]: $1.23r_c$ (Landau-de Gennes model) and from Lubensky *et al.* [131]: $1.19r_c$ (multipole expansion). For the elastic quadrupole we find the edge of the Saturn ring distortion at $1.28r_c$. Authors of Ref. [131] find the position of the defect ring edge at $1.08r_c$, whereas authors of Ref. [223] report $1.25r_c$.

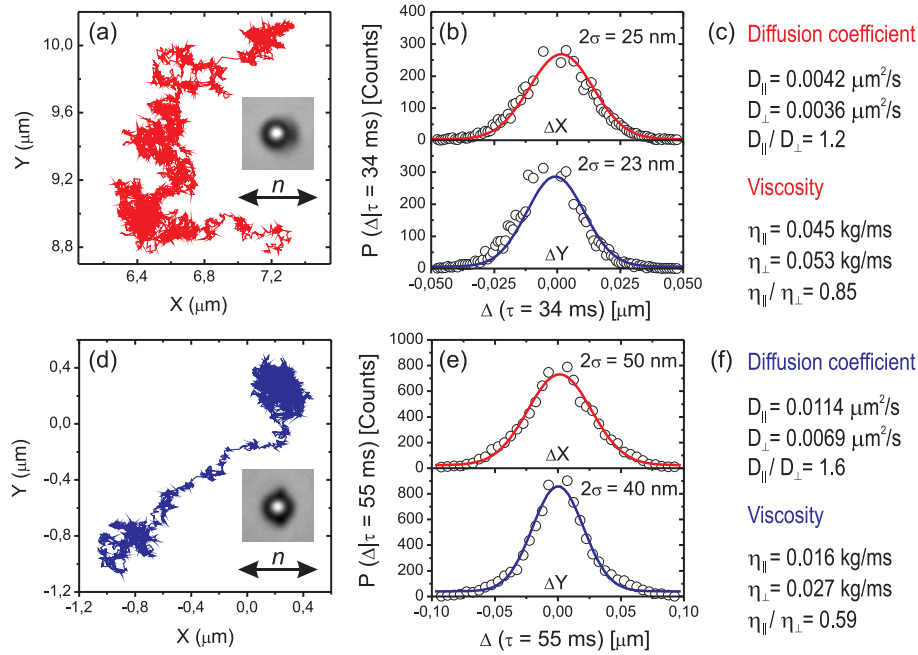


Figure 4.2: Brownian trajectories of $2.32 \mu\text{m}$ diameter homeotropic silica sphere embedded in a homogeneous nematic phase, inducing (a) dipolar or (d) quadrupolar elastic distortion. The time τ between two steps is equal to 0.034 s and 0.055 s , respectively. (b, e) Histograms of particle displacements along (ΔX) and perpendicular (ΔY) to the director $\mathbf{n}$ from a sample of 10000 trajectory steps. The red and blue solid lines correspond to the Gaussian fits. (c, f) Diffusion coefficients $D_{\parallel}$ and $D_{\perp}$, viscosity values $\eta_{\parallel}$, $\eta_{\perp}$ and anisotropy ratios derived from Brownian motion experiments.

Each colloidal sphere of radius r_c immersed in a fluid of viscosity η experiences a Stokes drag force $F_S = 6\pi\eta r_c v$, where v is the velocity of the particle [224]. For anisotropic liquids, an anisotropic drag force is predicted [225,226]. We have experimentally determined the Stokes drag coefficients of microsphere immersed in a nematic phase by following a Brownian motion experiment, similar

to Loudet *et al.* [227]. We studied a $2.32 \mu\text{m}$ diameter silica sphere with homeotropic surface anchoring, embedded in confined planar nematic liquid crystal, and thus exhibiting either dipolar or quadrupolar configuration at a certain cell thickness. Using video microscopy and particle tracking routines [144,207], it is possible to analyze the Brownian fluctuations and to obtain the particle positions at regular time steps. Typical trajectory of an elastic dipole, derived from 10000 snapshots taken every 0.034 s, is shown in Fig. 4.2(a). The self-diffusion coefficient of the fluctuating sphere is given by the Stokes-Einstein relation $D = \frac{k_B T}{6\pi\eta r_c}$, where k_B is the Boltzmann constant and T the temperature [122]. Since the nematic phase has a rotational symmetry axis, the Brownian motion is governed by two independent diffusion coefficients, namely $D_{\parallel}$ and $D_{\perp}$, which characterize the diffusive motion along and perpendicular to the director, respectively. They are expressed by $D_{\parallel/\perp} = \frac{k_B T}{6\pi r_c \eta_{\parallel/\perp}}$, where $\eta_{\parallel}$ and $\eta_{\perp}$ are related to the intrinsic viscosity coefficients of the liquid crystalline material [225,226]. From the analysis of Brownian fluctuations, it is possible to derive $D_{\parallel}$ and $D_{\perp}$. The probability that a particle will diffuse a distance Δ in the plane in time τ obeys the Gaussian distribution [122]:

$$P(\Delta|\tau) = P_0(\tau) \exp\left(-\frac{\Delta^2}{w^2(\tau)}\right), \quad (4.1)$$

where $P_0(\tau)$ is a normalization constant and $w(\tau) = 2\sigma$ is the width of the distribution. Averaging over 10000 steps, Fig. 4.2(b) shows the histograms of the particle displacements $\Delta = |\mathbf{r}(t + \tau) - \mathbf{r}(t)|$, where $\mathbf{r}(t)$ refers to the distance of the particle's center of mass to the origin of time t , in both $X(\parallel \mathbf{n})$ and $Y(\perp \mathbf{n})$ directions, respectively. The histograms are well fitted by a Gaussian distribution the width of which, w , is directly related to D through $w_{\parallel/\perp}^2 = 4D_{\parallel/\perp}\tau$. We see that $w_{\parallel} > w_{\perp}$, which implies that $D_{\parallel} > D_{\perp}$. It is therefore easier for elastic dipole to diffuse along the director than perpendicular to it. From the values of $w_{\parallel/\perp}$, one can calculate the anisotropy ratio $D_{\parallel}/D_{\perp}$, presented in Fig. 4.2(c).

The same experiment was performed also for the quadrupolar configuration [see Fig. 4.2(d-f)] and the obtained results are in fair agreement with results of the recent experiment performed by Loudet *et al.* [227] and Stokes drag computations, which take into account the distortions of the director field [225,226]. Finally, we have used the effective viscosity values $\eta_{\text{eff}} = \frac{1}{2}(\eta_{\parallel} + \eta_{\perp})$ for dipolar and quadrupolar configuration to estimate the attractive force $F(r)$ between two colloidal particles of radius r_c , initially separated by distance r . Since we have ascertained that the particle motion is viscously damped ($v < 1 \mu\text{m/s}$), the attractive force acting on the particle can be determined directly from the measured particle velocity v , following the Stokes law [136]:

$$F(r) = 3\pi\eta_{\text{eff}}r_c v. \quad (4.2)$$

4.1.2 Elastic dipole to quadrupole transition

One can traverse from elastic dipole to quadrupole by changing the effective confinement of the director field. This can be realized through several different approaches. Under the action of an external electric field, applied along the axis of the hedgehog point defect, an elastic dipole transforms to the elastic quadrupole [228,229]. Once the field is switched-off, the Saturn ring shrinks back to the hedgehog defect with an increasing velocity, showing that elastic dipole is more stable configuration in the given situation. Using a high-pressure technique, the simultaneous director configurational transition around a single microbubble has been observed, while its size was continuously changed [230]. When the size of the bubble has decreased by the applied pressure, a transition from elastic dipole to a Saturn ring configuration has occurred, as predicted theoretically [231]. The third example reports the direct observation of dynamical evolution of topological defects around bubbles rising due to the flow of nematic liquid crystal [232]. This time, the evidence for downstream convection of the Saturn ring and its transformation to a hyperbolic point defect as the velocity of the flow has increased, has been reported.

Surface confinement of a wedge-type planar cell has been used to observe either dipolar or quadrupolar Saturn ring configuration. Dipolar particles are observed in thicker parts of the cell, whereas particles of quadrupolar symmetry appear in more confined layers as illustrated in Fig. 4.3(a). This can be considered as if the tight planar confinement induces 'opening' of a point defect into a defect ring, which encircles the colloidal particle. The transition from dipolar to quadrupolar configuration is clearly visible under the microscope [see Fig. 4.3(b)], where the coexistence of both types is observed. This transition has been analyzed as a function of the local cell thickness by counting the number of each configuration at a chosen thickness. The distribution of director field profiles is shown in Fig. 4.3(c). In this particular case, the critical thickness h_c for 2.32 μm diameter silica spheres corresponded to 3.5 μm . The distribution is rather broad and the coexistence region fits to 1 μm variation of the local thickness.

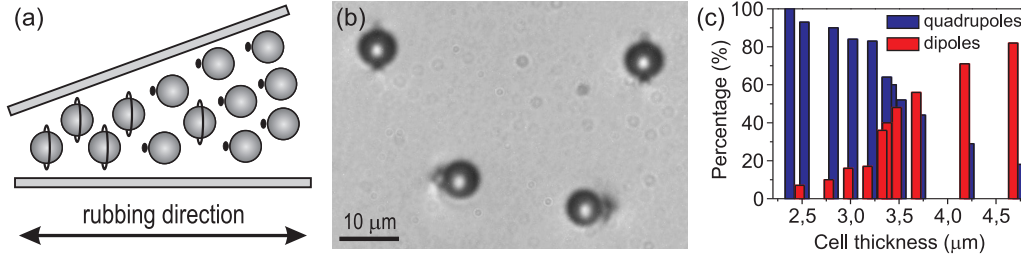


Figure 4.3: (a) In thinner parts of a wedge-type planar nematic cell, the particles with homeotropic surface anchoring adopt quadrupolar symmetry. In thicker parts, dipolar configuration prevails. (b) At a critical cell thickness, both types of symmetry are observed. Dipolar colloids have their point defects oriented along the rubbing direction, whereas quadrupolar colloids bear Saturn rings perpendicular to the rubbing direction. (c) Histogram represents the number of dipolar and quadrupolar particles at different cell thickness. Note rather broad region of the coexistence of both director field configurations.

4.1.3 Particle pairs

Using single particles to build multi-particle structures one should first start with particle pairs. The interaction between elastic dipoles and quadrupoles is highly anisotropic and interparticle potentials in the far-field regime follow the profiles calculated within the multipole approach. A pair of elastic dipoles in a uniform nematic fluid exhibits two stable configurations. Two parallel dipoles form a linear chain, as two antiparallel dipoles attract one another sideways, forming a tilted pair configuration. Both equilibrium configurations are presented in Fig. 4.4(a-f), together with polarized optical micrographs and the corresponding illustrations of the director field.

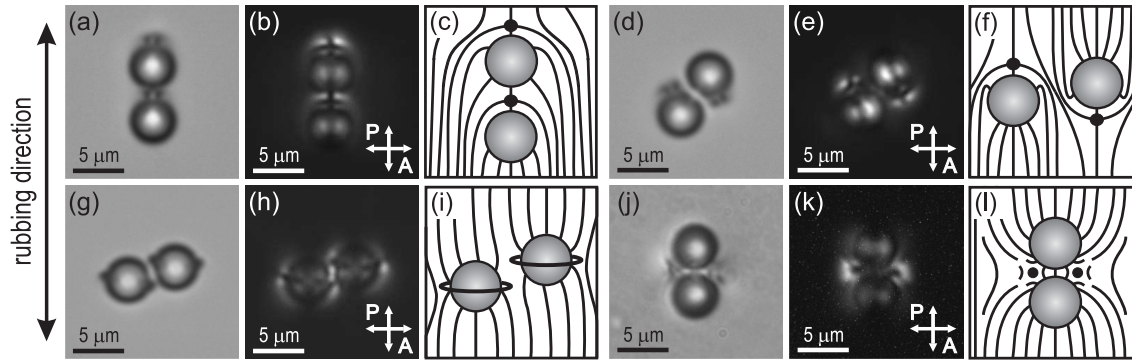


Figure 4.4: Particle pairs of elastic dipoles and quadrupoles. (a-c) Linear chain of two collinearly parallel dipoles. (d-f) Stable configuration of two antiparallel dipoles. (g-i) Stable configuration of two quadrupolar particles. (j-l) Bubble-gum configuration, where an escaped non-singular defect ring is situated between the particles. Director field is continuous everywhere and no counter-defects are present.

Quadrupolar colloidal pair has one stable configuration, presented in Fig. 4.4(g-i). Particles attract one another at an angle of 73° with respect to the far-field director. It is interesting to note how defect rings bend to minimize the total free energy. Additionally, one more exotic defect structure that accompanies two particles is occasionally, but regularly observed and shown in Fig. 4.4(j-l). It is considered as an escaped toroidal non-singular defect ring, situated between the particles [131,136,233] and popularly called the bubble-gum. Closely related, however, more stable configurations appear in chiral nematic colloids and they will be the topic of Section 5.2.

4.2 Two-dimensional nematic colloidal crystals

Assembly of colloidal particles into two-dimensional (2D) crystalline structures is studied. The work was initiated as a collaboration between experimentalists and theoreticians within our research group. The main result of this work is the evidence of existence of stable and long-range ordered nematic colloidal crystals in thin nematic layers. Two different types of 2D nematic colloidal crystals have been found in the experiments: those with dipolar and quadrupolar symmetry. The binding mechanism is the same in both cases and represents a fine balance between two basic effects. On one hand, the colloids minimize the total free energy of elastically distorted nematic liquid crystal by approaching each other and thus sharing topological defects with each other. On the other hand, when colloids are in close proximity, repulsive structural forces are generated because of strong spatial variation of the nematic order. Thus, a delicate balance between these two effects governs the positional and orientational ordering of 2D nematic colloidal crystals.

4.2.1 Assembly of dipolar colloidal chains

In early experiments, it has been observed that elastic dipoles spontaneously assemble into dipolar chains, with point defects all aligned in the same direction, as shown in Fig. 4.5(a-c). This kind of aggregation is well-known since first experiments of Poulin *et al.* [19,24] in water emulsions and has been studied extensively to date. Moreover, it has been observed that by increasing the concentration of colloidal particles, the dipolar chains form interesting local motifs and self-assemble into regions of quasi-ordered 2D structures, shown in Fig. 4.5(d). This observation was very strong indication that one could build long-range ordered colloidal structures in two dimensions under controlled assembly [80].

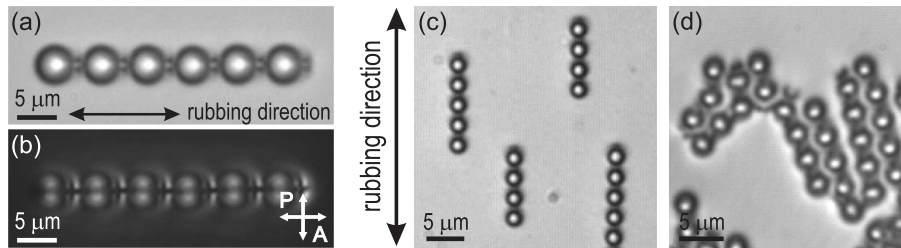


Figure 4.5: Aggregation of dipolar nematic colloids. (a) Colloidal chain of elastic dipoles observed under depolarized light and (b) between crossed polarizers. (c) Dipolar chains are spontaneously formed in appropriate concentration of nematic colloids. Adapted from Škarabot *et al.* [80]. (d) Spontaneous formation of 2D crystalline colloidal clusters.

The forces between two elastic dipoles in a homogeneous nematic field have been extensively studied before [19,24,51,52,78,136,208,234]. Similar experiments have been repeated using optical tweezers, where colloidal particles were initially positioned collinearly along the rubbing direction with hedgehog point defects oriented in the same or in the opposite direction, and released. In both cases, the long-range attractive interaction has been confirmed, resulting in strong binding potential of $5000 k_B T$ for $2.32 \mu\text{m}$ diameter colloidal particles.

In the next step, a method to switch the orientation of the dipole from one direction to the opposite has been developed. The method is based on local melting of small nematic region, surrounding the selected colloidal particle with optical tweezers [80]. The high-power laser focus was positioned on the colloidal particle, so that it was completely covered by the isotropic phase. Then, the optical trap was moved downwards and after switching-off the laser light, the defect was created in the position where the isotropic droplet shrank and disappeared.

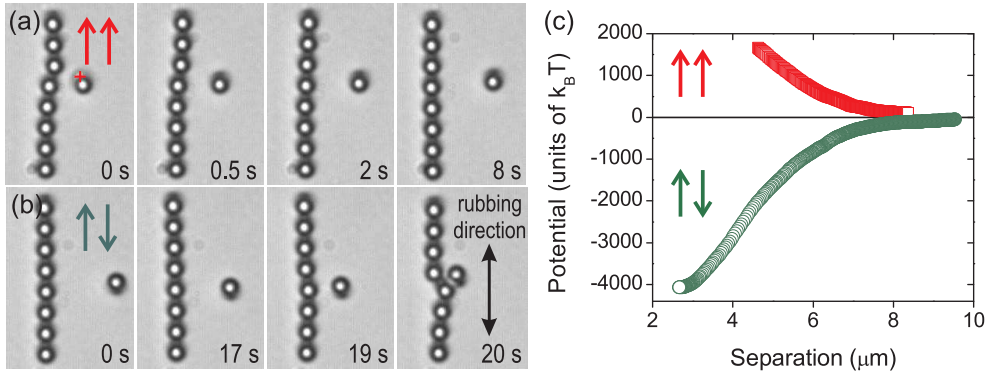


Figure 4.6: (a) For parallel orientation of the elastic dipoles and side position, the colloidal particle is repelled from the chain. (b) If the direction of the elastic dipole is reversed, the colloidal particle is strongly attracted to the chain. (c) Using the particle tracking software, the energies of repulsion (red data) and attraction (green data) between an isolated colloidal particle and dipolar chain were calculated. The experiment and the analysis was performed by M. Škarabot. Adapted from Škarabot *et al.* [80].

Reversal of the elastic dipole orientation with the 'melting-dragging' technique can easily be understood. An elastic dipole has a given orientation and in order to reverse it, one first needs to break the orientation, which is done by locally melting of nematic phase. At this stage the director field around the particle is symmetric with respect to the rubbing direction and therefore the relaxation to possible 'up' and 'down' states is energetically almost equally favorable. In order to favor one particular orientation, we need to discriminate these two possibilities, which we do by dragging the colloidal particle. The liquid crystal is molten only on the dragging side and thus, after switching-off the laser, the molten region acts as a source of the local disorder where hyperbolic point defect can form. The defect therefore always appears on that side of the particle, which is the last in contact with the isotropic droplet. This is an important step in the fabrication of ordered nematic colloidal structures.

Having control over the orientation of the dipolar particles, the forces between an isolated elastic dipole with the predetermined direction of point defect and a dipolar chain were further investigated. The structural force depends on the orientation of the elastic dipole, as clearly shown in two image sequences in Fig. 4.6(a, b). For the parallel orientation of dipoles, the colloid is repelled from the chain, whereas for the antiparallel orientation of dipoles, the colloid is strongly attracted toward the chain. This observation is crucial for further understanding of the stability of 2D dipolar colloidal structures in thin nematic layers. The strength of the attraction and repulsion was measured using video microscopy and particle tracking routines [144,207]. Having the recorded time dependence of the separation between the particle and the chain, the effective force acting on the particle has been calculated by Eq. (4.2). The product of the effective particle radius and viscosity $r_{eff}\eta$ has been determined in a separate Brownian motion experiment, described in Section 4.1.1. Finally, by integrating the force $F(r)$ over the separation r , the effective interaction potential between the particle and the chain has been determined. The results are shown in Fig. 4.6(c). As expected, the range of the interaction is long, reaching nearly 10 μm , and it is strong. It is necessary to deliver $\approx 4000 k_B T$ of energy to a single 2.32 μm dipolar particle to unbind it completely from the dipolar chain, assembled from eight colloidal particles.

Understanding of how the dipolar particles assemble into linear dipolar chains and knowing how to control the orientation of a single elastic dipole allows for directed assembly of large-scale nematic colloidal crystals. Figure 4.7 presents an example of 2D dipolar nematic colloidal crystal, assembled from 280 silica particles using optical tweezers. The stable crystalline structure consists of 9 shorter dipolar chains of 16 particles pointing downwards with their point defects and 8 longer dipolar chains of 17 particles pointing upwards with their point defects. Each dipolar chain can be considered as a topologically 'ferroelectric' object that attracts an oppositely oriented neighboring 'ferroelectric' topological chain, thus forming a topologically 'anti-ferroelectric' chain assembly.

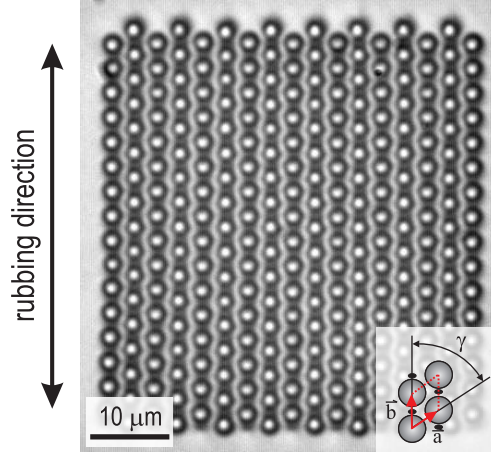


Figure 4.7: An example of 2D dipolar nematic colloidal crystal formed by pairs of antiparallel dipolar chains and assembled by M. Škarabot. The crystal consists of 280 silica particles and it is stable more than a year at laboratory conditions. The lattice vectors of the crystalline unit cell for $2.32\ \mu\text{m}$ diameter microspheres in $4.5\ \mu\text{m}$ thick planar cell correspond to $a = 2.95 \pm 0.03\ \mu\text{m}$, $b = 2.84 \pm 0.02\ \mu\text{m}$ and $\gamma = 61^\circ \pm 1^\circ$. Adapted from Škarabot *et al.* [80].

The details of the crystalline unit cell are shown as an inset in Fig. 4.7. It is a general parallelogram-shaped unit cell with the lattice constants $a = 2.95 \pm 0.03\ \mu\text{m}$, $b = 2.84 \pm 0.02\ \mu\text{m}$ and $\gamma = 61^\circ \pm 1^\circ$. In the case of $2.32\ \mu\text{m}$ diameter microspheres, this corresponds to $520\ \text{nm}$ surface-to-surface separation between colloids along the chains and $640\ \text{nm}$ separation between the nearest neighbors in sequent 'ferroelectric' chains. The crystalline structure is mechanically extremely robust and remained intact at laboratory conditions over the period of several months.

4.2.2 Quadrupolar colloidal clusters

The nature of the interactions among quadrupolar colloidal particles was systematically studied in order to understand their assembly into one-dimensional (1D) quadrupolar chains and 2D quadrupolar crystals. In the beginning, the investigation was concentrated on the spontaneous assembly of several quadrupolar particles, which led to some interesting structures, formed during the filling of the cell with nematic colloidal dispersion. Figure 4.8 shows some typical structures, observed at low density of the particles, where kinked quadrupolar chains, which have grown from a single quadrupolar pair, represent the dominating majority. However, in some cases, one can clearly observe quasi-ordered crystalline areas, such as the one in Fig. 4.8(d). This is a strong indication that 2D quadrupolar nematic colloidal crystals could be assembled as well, therefore we have focused on directed assembly with optical tweezers.

The interaction between an isolated quadrupolar particle and a kinked colloidal chain has been analyzed first. Using optical tweezers, individual colloidal particles have been trapped and positioned close to selected colloidal chain, as shown in the first two images of Fig. 4.9(a, b). The colloidal particles were further released and they approached along the chain direction. There

are two 'easy' directions for the colloidal binding to the already formed quadrupolar chain. Each of these directions forms an angle of 17° with respect to the average chain direction, which is itself perpendicular to the rubbing direction. In the first scenario, illustrated in Fig. 4.9(a), the colloidal particles formed a kinked quadrupolar chain with alternating directions of sequent colloidal particles. Alternatively, straight quadrupolar chains can be assembled, which are also tilted with respect to the rubbing direction, as shown in Fig. 4.9(b). In both cases, the binding energy is of the order of $1000 k_B T$, as illustrated in Fig. 4.9(d).

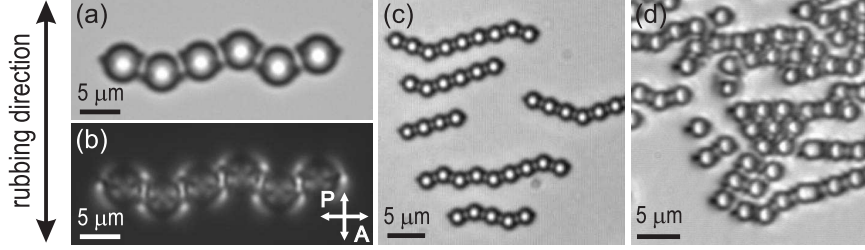


Figure 4.8: (a-c) A majority of self-assembled quadrupolar colloidal structures are kinked chains. Adapted from Škarabot *et al.* [81]. (d) However, in some parts of the sample, spontaneously ordered 2D quadrupolar crystallites are observed.

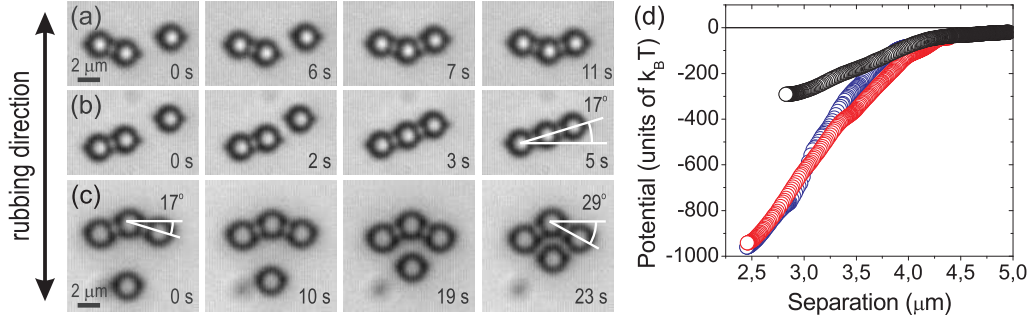


Figure 4.9: Quadrupolar chains can grow in the form of (a) kinked or (b) straight chains. (c) An isolated quadrupole is attracted laterally to the already formed quadrupolar triplet. The forming quadruplet is slightly distorted, as the kink angle increases to 29° . (d) The interparticle interaction as a function of separation between the released particle and the closest particle in the chain is close to $1000 k_B T$ (red and blue data). The lateral interaction is weaker and it amounts only to $\frac{1}{3}$ of the head-to-head interaction (black data). The experiment was performed by M. Škarabot. Adapted from Škarabot *et al.* [81].

Elastic quadrupoles do not only form chains but they also tend to form 2D regular patterns, presented in Fig. 4.9(c). Here, an isolated quadrupole was positioned close to the kinked chain (triplet) and released. When an additional quadrupole is incorporated and 2D quadruplet is formed, the angles among nematic bonds change significantly. Although the interaction is weaker in this case and it amounts only to $\frac{1}{3}$ of the head-to-head approach, it is still significant and drives colloidal assembly in 2D quadrupolar structures. It is important to note the principle of this observation, as it has allowed us to assemble large-scale quadrupolar nematic colloidal crystals using optical tweezers. For details see Mušević *et al.* [31] and Škarabot *et al.* [81].

4.2.3 Transport and crystallization of colloidal particles in an electric field

Massive colloidal transport and directed 2D assembly in a thin nematic layers on macroscopic scale can be realized via application of external AC electric field in a direction perpendicular to the nematic director. Previous observations have reported a steady drift of colloidal particles in transverse AC electric field [235–237]. Recently, the transport of charged colloidal particles has been observed when an in-plane DC electric field was applied in a nematic liquid crystal [49] and

unique orbiting motion has been reported in a smectic liquid crystal [238]. Using a combination of ITO coated glass with a $70\ \mu\text{m}$ gap between neighboring electrodes, we have created regions with no electric field and observed how colloidal particles are pumped from the region where the field is applied, into the region with no electric field. Uniform motion of $4\ \mu\text{m}$ big particles has been observed above a threshold value of $3\ \text{V}/\mu\text{m}$. Under the moderate amplitude and frequency, the particles were drifted steadily through the liquid crystal, whereas increase of the amplitude led to irregular motion at low frequencies. It is rather surprising that the particle motion was actuated only in a certain direction, despite the fact that director possesses $\mathbf{n} \rightarrow -\mathbf{n}$ symmetry. The latter implies an equal number of particles moving in $+$ as well as in $-$ direction, however, in our experiments almost all particles moved only in $+$ direction. We attribute this symmetry breaking to a slight director pretilt at the confining surfaces and splayed director field far and away from the particles, as illustrated in Fig. 4.10. To confirm this, we have prepared cells with parallel and antiparallel rubbing directions. When the rubbing directions on both confining surfaces were antiparallel, no macroscopic transport of the particles could be observed under applied electric field, whereas in cells with parallel rubbing directions, a massive transport of the particles was clearly evidenced in the direction opposite to the direction of rubbing.

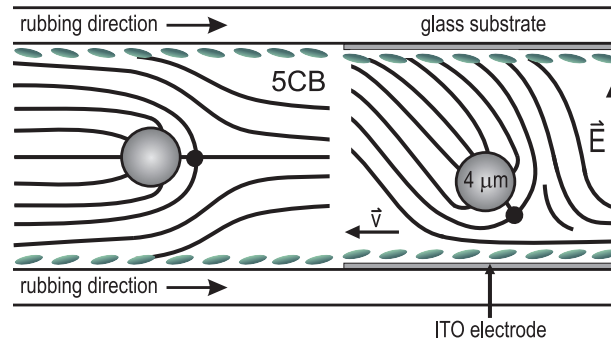


Figure 4.10: Schematic illustration of the experimental cell, filled with nematic colloidal dispersion. At zero electric field the nematic director is slightly splayed in the regions without colloidal particles (far left side), as the rubbing directions on both glass substrates are parallel. Above the Fréedericksz transition (right side), thin splayed nematic layer forms close to the electrode. Elastic dipole is oriented asymmetrically, with the hedgehog pointing toward the region of splay. Particle motion is observed in the plane perpendicular to the direction of electric field and drift velocity is opposite to the rubbing direction.

We consider that close to the 'field-no field' interface, the motion of colloids may be governed by a combination of electric field gradient force and the structural force. The electric polarizability of the particles was less than that of the medium, therefore they have to move towards the region of the lowest electric field. When the particle approaches the 'field-no field' interface, it is firstly accelerated and then pumped across the interface, as shown in Fig. 4.11(a). The transverse is quite rapid and the force exerted on a particle is very strong, up to $300\ \text{pN}$ for $4\ \mu\text{m}$ diameter particles [96]. After crossing the 'field-no field' interface, the particle is suddenly slowed down due to the elasticity of the medium and the absence of driving electric field gradient. More details of crossing the interface can be obtained from images taken between crossed polarizers [see Fig. 4.11(b, c)]. One can recognize that in the field region all colloidal particles appear spherically symmetric, accompanied with dark crosses. This means that the optical axis of the liquid crystal orientation around the particle is perpendicular to the plane of the image, indicating nearly uniform homeotropic alignment due to applied electric field. The hedgehog defect has turned into the field direction, which is most likely accompanied with opening of the point defect into a small ring, as already observed in the previous experiments [80,228]. Across the electrode edge, the individual particles have undisturbed dipolar configuration and all of them are oriented in the same way, with point defects staying behind the particles with respect to the direction of motion. The interface therefore acts as a kind of filter, which determines

the position of defects after the particle passage through the interface. We conjecture that the reason for this is an elastic distortion at the interface, which favors the sharing of defects.

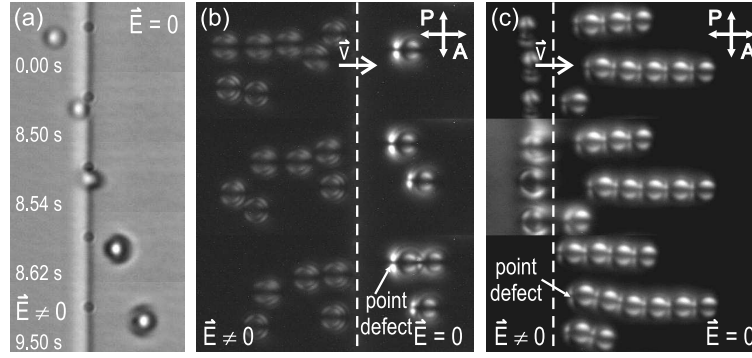


Figure 4.11: (a) Acceleration of a colloidal particle across the 'field-no field' interface. (b) The point defect stays behind the particle after traversing the interface, as can be clearly evidenced between crossed polarizers. (c) The density of the particles in the 'no field' region increases with time and linear dipolar chains start to form. The experiment was performed by M. Škarabot. Adapted from Škarabot *et al.* [96].

In the steady state, the applied electric field creates a steady transport of colloidal particles from the 'field' to 'no field' region. The particles are confined in that region by the high energy barrier and they are not able to escape. Consequently, the density of the particles in a planar region increases with time and they not only form dipolar chains, but also chains are forced to approach each other and to form more dense 2D structures. At higher particle concentrations the chains spontaneously dissociate and nematic bonds are formed in random combinations. The time evolution is shown in Fig. 4.12(a, b), where two distinct regions of the colloidal crystal growth are indicated. In the region 'A', the density of colloidal particles is too low to induce condensation of chains into crystallites, whereas in region 'B', a dense crystalline structure is formed. It should be mentioned that in the process of filling up the 'no field' gap, the particles inside the gap also migrate in direction perpendicular to the drift velocity. Figure 4.12(c) shows an enlarged area, where a dense 2D lattice has formed. Each colloidal particle is accompanied by two dark spots, which correspond to projection of the Saturn ring. This is a clear indication that during the process of crystalline structure formation, point defects open into Saturn rings, thus providing enough space for other particles to come closer to each other.

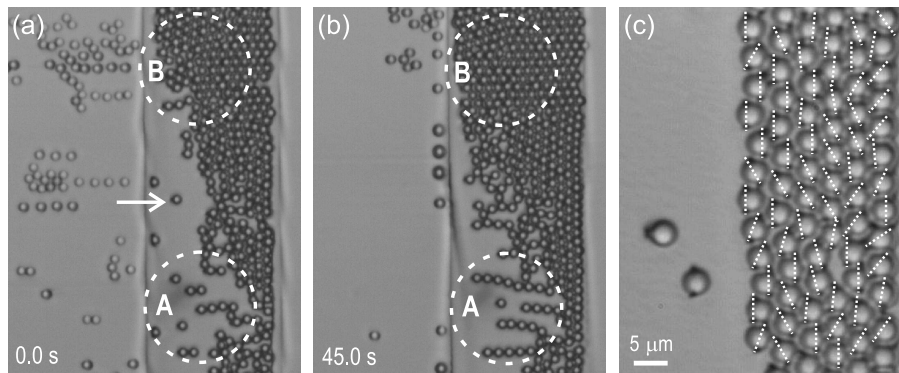


Figure 4.12: (a, b) Formation of a dense 2D nematic colloidal crystallite. (c) Randomly assembled hexagonal structure is shown at higher magnification. Dark spots are projections of Saturn rings encircling the colloidal particle in a thin nematic layer. White lines are added to illustrate the orientation of the Saturn ring. The experiment was performed by M. Škarabot. Reprinted from Škarabot *et al.* [96].

Similar effects have been observed also in other experiments [228,229,234]. Using ferromagnetic colloidal particles, Noël *et al.* [234] were able to press two dipolar particles to very small separation (≈ 20 nm) using an external magnetic field, allowing them to observe how the point defect

opens into the Saturn ring. The force required to induce such a distortion is ≈ 3000 pN, which is an order of magnitude larger than the force we have measured across the interface. However, our cells were thin and the confinement has certainly reduced the energy barrier between dipoles and quadrupoles. More precise measurements of the separation dependence of the structural force between an atomically flat mica sheet and a micrometer-sized glass sphere, immersed in the nematic fluid, were performed in our laboratory using the atomic force microscopy [239]. We have shown that below a threshold thickness (≈ 4 nm) of a hybrid nematic layer with a topological defect an eigenvalue exchange transition occurs and the defect is squashed flat into a biaxial layer [240–242]. The surface anchoring was namely so strong that the eigenvalue exchange has played the role of the surface anchoring breaking. We are confident that similar transition generally occurs in experiments that involve defect-mediated interactions of sub-micrometer colloids in anisotropic fluids, where the conditions of extreme confinement are expected.

The combination of two presented effects, colloidal drift under applied electric field and particle pumping across the 'field-no field' interface, leads after some time to the formation of compact crystalline structures (see Fig. 4.13). The analysis of the formed structure has shown that we always obtain 2D hexagonal lattice, however, the unit cell can have different angle of orientation with respect to the rubbing direction. As indicated in Fig. 4.13(b, c), the unit cell is in different parts of the crystal rotated by an angle, which is in the range between 30° and 36° .

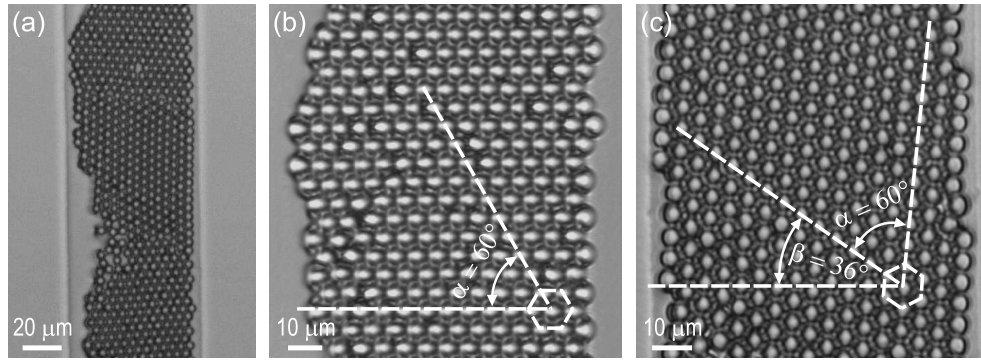


Figure 4.13: (a) Hexagonal crystallites, formed in the gap, have different orientation with respect to the electrode edge. (b, c) Enlarged areas of (a), show two distinct orientations of the hexagonal lattice. The experiment was performed by M. Škarabot and analyzed by myself. Reprinted from Škarabot *et al.* [96].

We have also investigated the temporal stability of 2D crystalline structures. In some cases, the crystallite was stable for several days, while in other cases, it was soon disrupted by external stimuli, such as inevitable liquid flow due to temperature changes. However, if we heated the nematic fluid into the isotropic phase, topological defects disappeared and the colloidal crystallite rapidly disintegrated due to enhanced Brownian motion. This is a clear evidence, that in the nematic phase, the elastic distortion provides some binding forces between colloidal inclusions, which is in fair agreement with our previous observations [31,81]. Recently, it was demonstrated that 2D quadrupolar nematic colloidal crystals are stable, but highly susceptible to external stimuli, which often disrupts the established order [81]. In the present case, an additional reason for the observed fragility of the colloidal assemblies might be in relatively bad uniformity of the colloidal surface properties. Namely, in many cases, we have observed that among quadrupolar also dipolar particles have appeared, that disrupt the order in 2D quadrupolar crystal.

The exact mechanism of the presented colloidal transport is not clear at the moment and should be the subject of a detailed theoretical study involving hydrodynamics of liquid crystal. However, it is quite evident that such robust control is scarce and limited for achieving regular and tunable colloidal architectures. Therefore, more efforts regarding the massive organization of nematic colloids are directed in the recent breakthrough about robust chemical control of colloidal self-assembly at liquid crystalline interfaces [43,243].

4.3 Entangled colloidal structures

4.3.1 Metastability and temperature quench

Liquid crystal organization around colloidal particles may adopt a variety of different configurations at chosen external parameters, like confinement, external fields, surface anchoring and particle size. An example of such coexistence is presented in the previous Section, where both dipolar and quadrupolar colloidal structures have been assembled at very similar conditions. The stability of a particular colloidal configuration depends primarily on its total free energy and also on external parameters, such as material flow, temperature profile, domain walls and kinetics of topological defects. The external parameters can energetically favor a particular structure during its formation, for instance the assembly of linear dipolar chains when colloidal dispersion is filled in the planar nematic cell. In general, the energy scale of nematic colloids greatly exceeds thermal energy of several $k_B T$, and therefore the frequency of occurrence of a particular configuration is not determined by the Boltzmann distribution. This should be taken into account when building complex colloidal structures in anisotropic fluids.

To achieve the nematic relaxation that starts from the disordered state, a fast temperature quench from isotropic to nematic phase should be used. In the 1990s, studies of defect annihilation were stimulated by astrophysical analogy between the liquid crystal and cosmological defects [128,244]. Here the exact dynamics of defect formation will not be of central importance since we use the sudden phase transition only as a tool to organize and access energetically less favorable but topologically allowed complex nematic defect configurations. Experimentally, this can be performed by optical tweezers due to their ability to produce localized and controlled heating. After the laser beam locally melts the nematic liquid crystal into the isotropic phase, the tweezers are switched-off. Instantaneously, domains with randomly oriented nematic ordering start to form. Over a time the degree of order in the domains increases and so does their size. Optical micrographs of such defect evolution are shown in Fig. 4.14(a). The 'zoo' of randomly oriented $+\frac{1}{2}$ and $-\frac{1}{2}$ defect lines looks like spaghetti, which later in the relaxation process simultaneously annihilate and finally disappear. Consequently, the uniform configuration with the lowest free energy and a zero topological charge is established in an empty nematic cell.

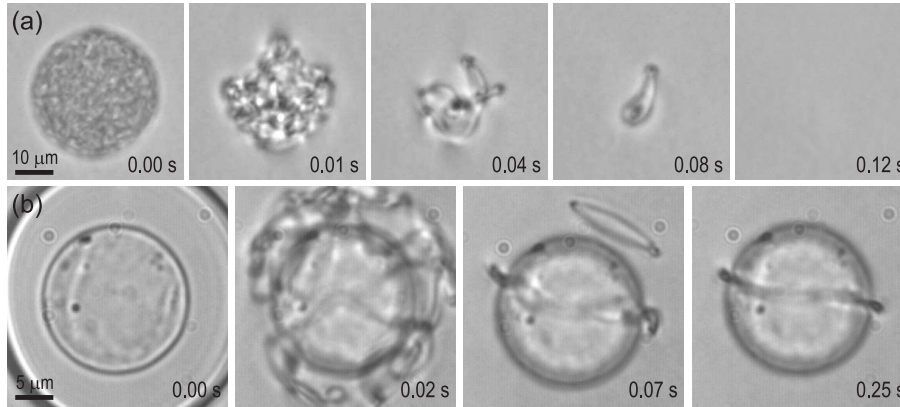


Figure 4.14: (a) Temperature quench of a 12 μm thick nematic layer. The heating into the isotropic phase is provided by absorption of laser light in the ITO layer on the inner side of the substrate, which is in contact with liquid crystal. The zoo of randomly oriented $+\frac{1}{2}$ and $-\frac{1}{2}$ defect lines is generated instantaneously after switching-off the laser and few moments later all of them simultaneously annihilate and finally disappear. (b) When temperature quench is performed around a single spherical particle, one single defect loop remains, while all others annihilate. The experiment was performed by M. Škarabot.

The situation is different when colloidal inclusions are introduced. In the case of single homeotropic spherical particle, a dipolar configuration with hedgehog point defect or a quadrupolar Saturn ring configuration has to appear after fast temperature quench [81], as demonstrated in

Fig. 4.14(b). However, there is much more interesting situation with different scenarios when the liquid crystal around two colloidal particles is quenched. Defects are unable to relax completely because they are hindered by the presence of particles. Therefore metastable configurations can arise, where complex defect loops entangle several colloidal particles.

4.3.2 Entangled colloidal pairs

Optical tweezers were used to assemble entangled particle pairs in nematic liquid crystal. Using high intensity laser beam, the nematic phase was locally heated around the selected colloidal particles into the isotropic phase and then quenched back to the nematic phase by switching-off the light. Figure 4.15 presents the time sequences of depolarized optical micrographs, showing the formation and the entanglement of topological defects around two $19\text{ }\mu\text{m}$ big colloidal particles after temperature quench. In a fraction of a second, a new topologically stable object, with single $-\frac{1}{2}$ defect line, encircling both particles in the form of a twisted loop, is created [see Fig. 4.15(a)]. This structure is known as the *figure of eight* [14,83]. The disclination line starts in front of the first particle, sinks below the second, comes from behind to frontage of the second, sinks below the first, and finally from behind of the first particle connects into a loop.

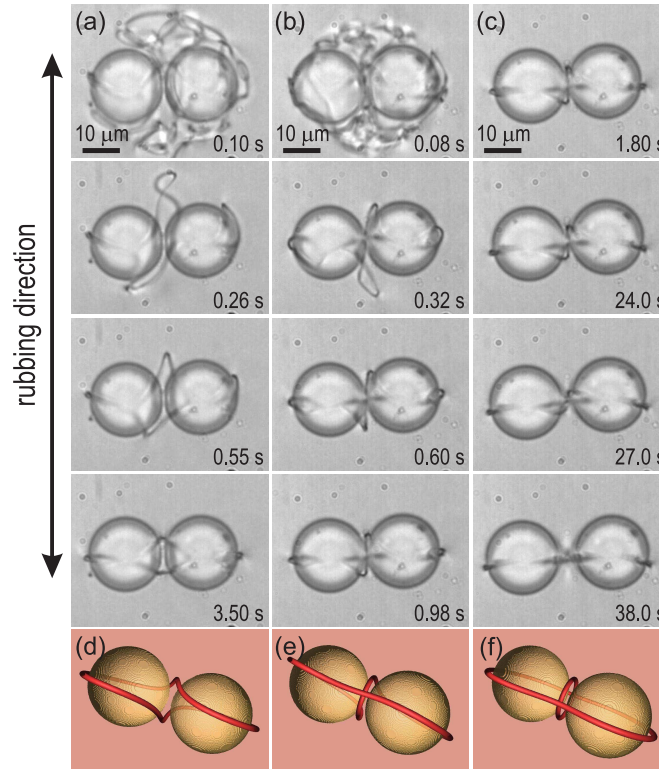


Figure 4.15: Assembling entangled colloidal pairs by temperature quench using the focused laser light. The diameter of the particles corresponds to $19\text{ }\mu\text{m}$, the cell thickness is close to $21\text{ }\mu\text{m}$. (a) Figure of eight entangled state. The disclination loops are visible under depolarized optical observation due to the scattering of light. (b) Evolution of the figure of omega entangled state. (c) The figure of omega is metastable and transforms slowly into entangled point defect. Numerical analysis of the creation process of the entangled colloidal states was performed by Landau-de Gennes tensorial approach and accomplished by M. Ravnik [8]. Just like in the real experiment, the defect lines condensed around two particles in a form of (d) figure of eight, (e) figure of omega and (f) entangled point defect [222]. The experiment was proposed by I. Mušević and performed by M. Škarabot. Adapted from Ravnik *et al.* [83].

Besides the figure of eight, two other types of similar binding have been observed in experiments. Figure 4.15(b) presents the formation of a more complicated, asymmetrically entangled single disclination loop, which we call the *figure of omega*. In contrast to the figure of eight, the figure

of omega has a straight defect line at the front side, which sinks behind both colloidal particles and makes an additional loop between them. This additional loop resembles a Greek letter Ω if looked at along the particle pair. In most experiments this configuration is unstable and transforms slowly into another more stable configuration, shown in Fig. 4.15(c). We call it the *entangled point defect* because it consists of two separate $-\frac{1}{2}$ defect rings, which are oriented perpendicularly one with respect to another. The larger defect ring winds around both particles and stabilizes them into a stable entangled object. The inner smaller ring is effectively a -1 hyperbolic point defect with an escaped core. In terms of entanglement, it is a 'bystander' as it only locally relaxes the director field. Figure of eight and figure of omega are chiral objects as they break the mirror symmetry. The structures with left or right handedness are equally probable and have the same energy in homogeneous nematic field. The degeneracy of the two structures can be lifted in a non-homogeneous preferential nematic ordering, for example in 90° twisted nematic cell. Observing such spontaneous formation of chiral objects in achiral medium is highly interesting and could be exploited for applications in optics.

It should be stressed that entangling colloidal particles through the temperature quench is a stochastic process, where particular entangled structure forms only with a certain probability. Indeed, when performing a set of quenches, one observes that only in roughly half of relaxations an entangled defect configuration forms, whereas in the other half two quadrupolar particles with encircled Saturn ring are generated. Out of 124 quenching experiments, 52 % of the final states were entangled, precisely 36 % were figure of eight, 13 % were figure of omega and only 3 % directly relaxed into entangled point defect. More detailed analysis of temperature quench in the vicinity of colloidal particles has shown that the size of the quenching volume plays an important role. If the temperature quench embraces both particles and the liquid crystal is heated into the isotropic phase, the defect formation is purely stochastic. However, the more precise control over the realization of the final configuration can be obtained by the quench of a smaller volume.

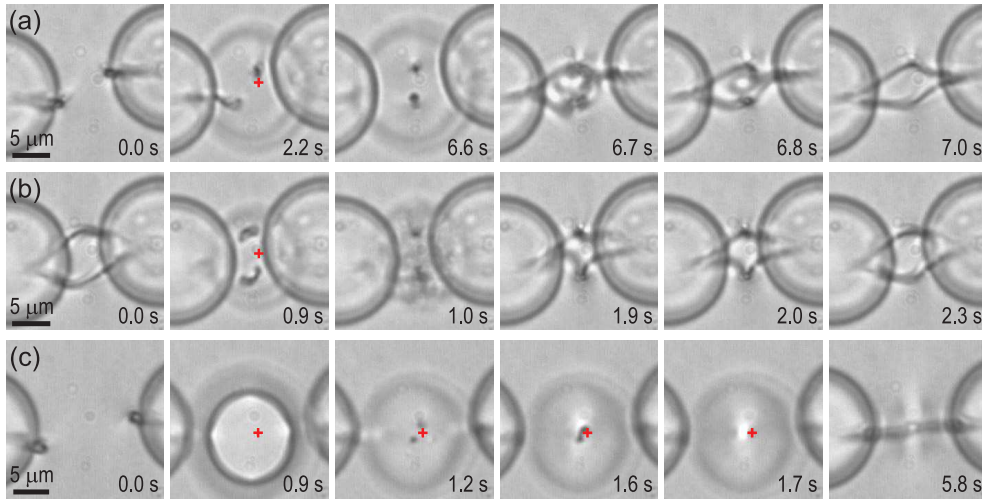


Figure 4.16: Entangled colloidal structures can be assembled from locally heated nematic volume in a controlled way. (a) Figure of eight entangled state is formed from two coiled-up defect strings, which rapidly disentangle and reconnect the remnant parts of the Saturn rings after switching-off the trap (red cross). (b) The formation of figure of eight is reversible if one precisely controls the size and strength of the temperature quench. (c) Entangled point defect can be obtained at higher trapping power when two $-\frac{1}{2}$ defect strings likely join into -1 hyperbolic point defect before relaxing into the final entangled state. The experiment was performed by M. Škarabot and analyzed by myself.

Figure 4.16 shows a closer inspection of three localized temperature quenches. In Fig. 4.16(a), an intermediate volume of nematic liquid crystal is slowly heated close to the nematic-isotropic phase transition, which causes detachment of short defect line segments from the surface of the

particles. These segments are curled-up into separate strings, visible as two black spots in the middle of the heated area. We assume that these are the embryos of a $-\frac{1}{2}$ defect line. When an optical trap is switched-off, these coiled-up defect strings suddenly disentangle and rapidly join with the remnant parts of the Saturn rings, forming the figure of eight entangled state. Sequence of optical micrographs in Fig. 4.16(b) shows a similar course of events, starting and finishing up with the same entangled configuration. It is important to mention that now one has the prevailing control over the final entangled state formation due to avoiding the complete erasure of the initial state and due to the gentle tuning of trapping power. The third example, shown in Fig. 4.16(c), demonstrates controlled arising of entangled point defect from slowly cooling of locally isotropic phase. Two defect strings likely join into a -1 hyperbolic point defect, which sits in the middle of longer defect line, winding around both colloidal particles.

4.3.3 Binding potentials and topology of entangled defect loops

The three entangled colloidal pairs share similar properties, namely that a closed $-\frac{1}{2}$ defect loop winds around two particles and thus arrests them into a new joined object, which proves to be highly robust and stable. The strength of entanglement was measured by switching-on two separated optical traps and grabbing two $4.72 \mu\text{m}$ diameter microspheres at their opposite sides. The entangled pair was stretched by moving both traps in the opposite direction to a predetermined position, and then the trap was switched-off [83]. Interestingly, the entangled defect loop acts as an elastic string, pulling both particles together. String-like interaction between a pair of nematic colloids was reported earlier for binding with an escaped hyperbolic ring before [136,233].

From the recorded images the effective force and the binding potential of the entangled line defects were determined as a function of separation. As the force does not depend significantly on separation, the binding potential is to some extent linearly proportional to the interparticle separation r . It yields an extremely strong effective colloidal interaction, of the order of $10000 k_B T$ for $4.72 \mu\text{m}$ diameter spheres [83]. Such binding is thus by an order of magnitude stronger when compared to non-entangled structures of elastic dipoles and quadrupoles. The string-like binding potential of entangled particle pairs can be explained qualitatively by considering the increase in disclination lengths when stretching the whole entangled structure. Free energy F_{DL} of a straight $-\frac{1}{2}$ defect line is linearly proportional to the length l of the defect line $F_{DL} = W_{DL}l$, as introduced in Eq. (2.26). By estimating $\ln(\frac{R}{r_c}) = \ln(\frac{500 \text{ nm}}{10 \text{ nm}}) \approx 5$ and assuming an isotropic defect core ($W_c = 0$), one obtains $F_{DL} = \pi K l$. This simple estimate shows that the interaction potential between particles bound by entangled defect lines is indeed string-like if the change in the nematic profile is primarily due to the increase of the linear defect regions. Nevertheless, at close particle separations, where disclination lines not only stretch but also reposition, twist and bend, such linear scaling of the free energy fails.

By addressing entanglement using topology, entangled defect structures are characterized by their topological charge q . Topological charge is defined as an integral over a closed defect-less surface (see Section 2.5). Usually, topological charge is ascribed to point defects, but topologically they are equivalent to connected defect loops if the director field of one configuration can be continuously transformed to the other. Thus, in terms of topology, entangled structures are combination of colloidal particles and entangled defect lines. Homeotropic colloidal particles generate perturbations of the nematic field equivalent to radial hedgehogs and thus each carry an effective positive charge $+1$ [129,130,138]. The experiments demonstrate that entangled defect lines compensate the radial perturbation of particles by generating hyperbolic defect regions, which have a negative topological charge. When building entangled colloidal structures in an uniformly aligned nematic field, one sets a constraint that the topological charge induced by particles must be exactly opposite to the charge induced by entangled defect lines. Indeed, if using uniform director $\mathbf{n} = \text{const.}$ in Eq. (2.27), spatial derivatives of $\mathbf{n}$ give total charge $q^{\text{tot}} = 0$.

This can only be realized if:

$$q^{\text{tot}} = q^{\text{par}} + q^{\text{def}} = 0 \quad \rightarrow \quad q^{\text{par}} = -q^{\text{def}}, \quad (4.3)$$

where q^{par} is the net topological charge induced by particles and q^{def} the net topological charge induced by entangled defect lines. Finally, having an uniform field with zero topological charge, perturbed by two spherical particles, each carrying $+1$ topological charge, gives the charge of the entangled defect structure -2 to compensate: $-2 = -(1 + 1)$.

4.3.4 Entangled colloidal chains and nematic braids

The entanglement is not necessarily limited only to particle pairs, but can be extended over many particles, forming linear entangled chains. In Fig. 4.17(a), a chain, based on the figure of eight configuration is presented, where a single defect line is winding around all particles and has the topological properties of a higher integer value point defect. Such chains are chiral objects and can be either left or right-handed. There is also no a priori limitation for assembling a chain with both left and right-handed links in homogeneous nematic field [222]. Colloidal chain of entangled point defects is shown in Fig. 4.17(b). Here, the chain can be locally considered as a simple arrangement of elastic dipoles, for the first time observed in early experiments by Poulin *et al.* [19], where the last defect transforms in a closed loop that encircles the whole chain. Consequently, the direction of the chain is rotated by 90° perpendicular to the non-distorted nematic orientation.

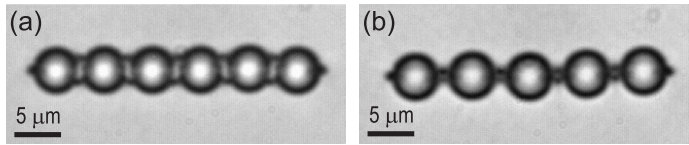


Figure 4.17: Entangled colloidal chains, assembled from $4.72 \mu\text{m}$ diameter silica particles. (a) Chain based on the figure of eight. (b) Chain of entangled point defects. The average equilibrium surface-to-surface separation between the neighboring spheres corresponds to $1.06 \mu\text{m}$ in (a) and $1.10 \mu\text{m}$ in (b). The experiment was performed by M. Škarabot. Adapted from Ravnik *et al.* [83].

Topologically, entangled chains are characterized by generalizing the results for the entangled colloidal pairs. Single defect line in the figure of eight manner winds here not only around two but in general around N particles, where experimentally $N = 5, \dots, 20$ can be easily realized. For such entangled defect loop an uniform orientation of the nematic at the substrates defines its topological charge equal and opposite to the topological charge imposed by the particles $q^{\text{def}} = -N$. Being able to build linear entangled objects, there is another generalization of entanglement phenomena to 2D or even three-dimensional (3D) colloidal structures, called the *nematic braids* [85]. The procedure and arguments for entangling more-dimensional colloidal objects should be the same as for linear chains, only that substantially more conformations can exist in higher dimensions. Recent numerical calculations have confirmed 2D entanglement of colloidal clusters and periodic crystals [85]. Unfortunately, most of those conformations are metastable and quite susceptible to disturbance of particle positions, therefore small differences in their free energies make them fragile for manipulation and assembly. This should be the main reason for unsuccessful experimental realization of 2D entangled colloidal structures in homogeneous nematic field. External fields with suitable symmetry or geometrical stimuli are therefore needed to favor particular conformations and allow their assembly into neatly entangled colloidal crystals.

Results and discussion

In this Chapter the main results of the thesis are presented. They are organized in three separate Sections, which report my original work. The first part is devoted to interactions of microrods in uniform nematic fields and it was originally published in Tkalec *et al.* [35]. The second Section represents experimental studies of vortex-like defect rings in chiral nematic colloids. It was originally published in Tkalec *et al.* [97]. The third Section of this Chapter demonstrates that knots and links of various complexity can be realized and arbitrary reconfigured by optical manipulation of delocalized defect lines in confined chiral nematic colloidal dispersion.

5.1 Interactions of microrods in uniform nematic fields

In this Section we present an experimental analysis of topological properties of nematic liquid crystal ordering in the vicinity of colloidal rod-like inclusions. The glass microrods disturb the uniform alignment of the surrounding nematic host, resulting in both a distinct equilibrium alignment and highly directional pair interactions. Depending on the equilibrium orientation of the object and the strength of confinement, we have observed either dipolar or quadrupolar symmetry of elastic distortion. Using precise optical tweezers manipulation, the strength and the separation dependence of various interparticle forces have been determined. Our results are in agreement with previous theoretical calculations and they represent the first experimental investigation of structural morphologies around anisotropic objects in confined nematic liquid crystal.

5.1.1 Director field configurations around individual microrods

For increasing the complexity and diversity of colloidal architectures, the generation of new building blocks and emergence of anisotropic interactions is necessary [245]. While spherical particles in a nematic host already offer a splendid variety of structures, anisotropic objects, from glass microrods to carbon nanotubes, can provide even more opportunities for the formation of self-organized structures [25]. Over the past few years, several theoretical studies have been reported, addressing the orientation of individual cylinders [246], defect structures and torques on an elongated objects in the nematic solvent [247–249], as well as predicting the interactions between anisotropic particles in confined nematic fluid [250–254]. Most of them were restricted to two-dimensional (2D) problems and the respective analyses were performed either using molecular dynamics simulations [250], density functional theory [251,252], or Landau-de Gennes tensorial approach in three dimensions [253,254]. On the other hand, there is a lack of detailed experimental studies of the director field symmetry around cylindrical inclusions and systematic studies of pair interactions between rod-like particles in nematic dispersions are lacking as well. This can be partially understood by taking into account the low availability of appropriate material in the micrometer range and knowing that detailed observations under an optical microscope are especially difficult to perform with much smaller nanoparticles [46–48,255–257]. However, the symmetry and general properties of the interaction potentials between rod-like particles in the nematic fluid should not depend on their size, but are to the greatest extent determined by their

surface anchoring properties. This means that the interaction between cylindrical particles could be determined on relatively large, micrometer-sized objects, and then these properties could be extrapolated down to the nanometer scale [239,258]. This is a powerful approach for predicting the physical properties of nematic colloidal dispersions at very different length scales.

We have used rod-like glass particles of $1.5\ \mu\text{m}$ diameter, several micrometers long, with strong homeotropic surface alignment for the surrounding 5CB nematic liquid crystal (see Section 3.1.1). These microrods are manufactured by cutting alkali-free glass fibres and are mainly used as gap-spacers in liquid crystal displays [6]. Whereas the diameter distribution of the particles is very precise, less is known about their length distribution. We have therefore performed measurements of microrods length by depositing them on a clean surface and measured the length of a large number of particles under an optical microscope. The results are shown in Fig. 5.1(a). The distribution of lengths is quite broad and it is centered around $8\ \mu\text{m}$, giving a typical aspect ratio of 1 : 5.

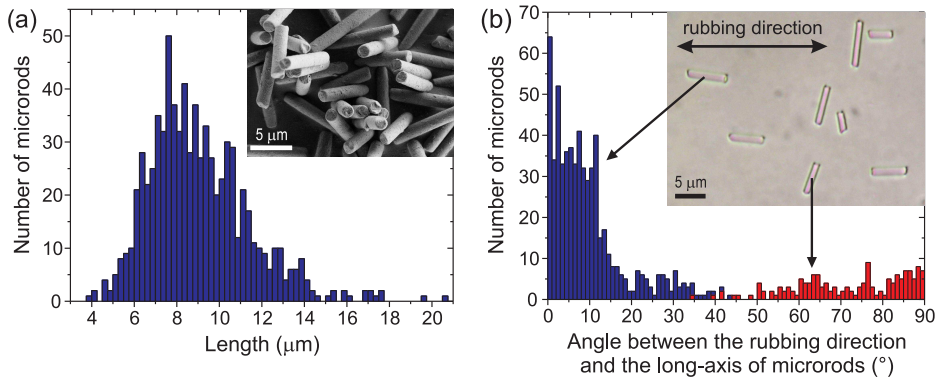


Figure 5.1: (a) Distribution of lengths of $1.5\ \mu\text{m}$ diameter microrods, as determined by measuring the length of 660 particles under an optical microscope. SEM micrograph of the particles is shown in the inset. (b) Distribution of angles between the rubbing direction and the long axis of microrods. The blue color represents the majority of microrods orientations, almost coinciding with the rubbing direction, whereas the considerable number of particles, shown in red color, is oriented almost perpendicularly to the rubbing direction. The cell thickness was close to $4\ \mu\text{m}$. Adapted from Tkalec *et al.* [35].

Further, we have analyzed the orientation of microrods in a planar nematic cell, as can be observed in a freshly prepared sample. Figure 5.1(b) shows a distribution of spontaneously oriented $1.5\ \mu\text{m}$ diameter microrods in a $4\ \mu\text{m}$ thick layer of 5CB. The majority of inclusions has oriented along the rubbing direction (blue data) and the angular width of the distribution corresponds to $\approx 10^\circ$. Moreover, considerable number of microrods has oriented in a wide interval from 60° to 90° with respect to the rubbing direction (red data). This indicates that nematic liquid crystal alignment around differently oriented microrods might create different structural morphologies, therefore we have focused on analysis of the director deformation around individual inclusions.

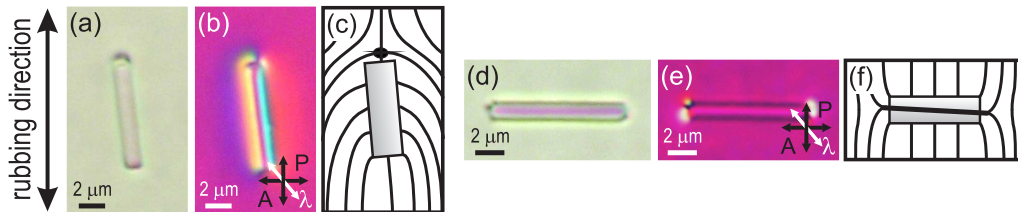


Figure 5.2: (a-c) Microrods of dipolar symmetry in thin planar nematic layers, as observed under polarizing optical microscope. When a λ plate is inserted, the differently colored regions indicate different orientations of nematic molecules. The director pattern can be easily reconstructed from the colors. (d-f) Quadrupolar microrod in a thinner part of the cell is oriented perpendicularly to the rubbing direction. (f) Illustration of the director field is deduced from (d) depolarized and (e) colored optical micrographs.

Topological details of the director pattern around homeotropic microrods are revealed using the polarizing optical microscopy. We have observed that there are only two characteristic types of director configurations, which are shown and illustrated in Fig. 5.2. The first kind of director pattern is similar to the dipolar pattern in nematic colloidal dispersions of microspheres, as shown in Fig. 5.2(a-c), and we call it a *dipolar microrod*. Figure 5.2(a) shows a depolarized micrograph of a dipolar microrod, where the point defect is located on top-end of the rod. The director orientation is best illustrated in the color micrograph, taken between crossed polarizers with inserted red plate [see Fig. 5.2(b)]. The red color corresponds to a vertical orientation of the long axes of the molecules, whereas bluish and yellowish colors correspond to clockwise and anticlockwise rotation of the director, respectively. This enables us to reconstruct the director pattern around the selected microrod, which is schematically illustrated in Fig. 5.2(c).

The result is not surprising if we consider the topological aspects, which are responsible for the resulting symmetry of the director field pattern around the microrod. Namely, the conservation of the topological charge [21,129] requires that the net topological charge of the system remains unchanged whenever an inclusion is introduced into homogeneous nematic field. Topological defect, which must be created in the vicinity of inclusion, is topologically equivalent to the radial hedgehog, located inside the inclusion. It is important to note that the shape of the particle in this case does not matter at all. Therefore the microsphere is in this sense topologically equivalent to the microrod. In short, for homeotropic surface anchoring they both represent a radial hedgehog, which is the source of the director distortion. This conclusion is very important and allows us to predict that similarly to the spherical nematic colloids, we can expect that microrods of quadrupolar symmetry should appear in our samples as well. They have been indeed observed in our experiments and one example is presented in the sequence of images in Fig. 5.2(d-f). Note the difference between the general orientation of the microrods in Fig. 5.2(a) and Fig. 5.2(d). Whereas the dipolar microrod is oriented along the rubbing direction of a planar nematic cell, the *quadrupolar microrod* is spontaneously oriented perpendicularly to the rubbing direction. A tiny thread, located on the rod and running from the left to the right end of the particle can be revealed from the depolarized image in Fig. 5.2(d). This is a signature that the hedgehog point defect on the top of the rod has opened into the Saturn ring, encircling the microrod along its longer axis [21,253]. The situation is topologically equivalent to the well-known observation of Saturn rings in the nematic dispersion of microspheres and it confirms our original conjecture, that the shape of the inclusion does not matter on global scale.

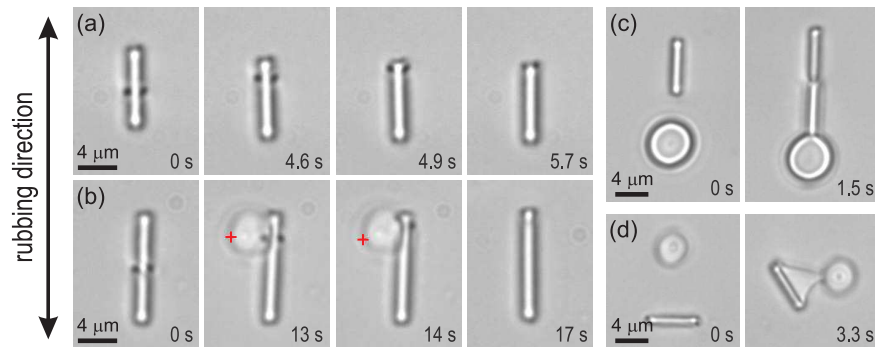


Figure 5.3: (a) Using optical tweezers, one can force the point defect of the dipolar microrod to open into a Saturn ring, visible in the middle of the rod. This position of the ring is unstable, therefore the ring slips back to the point defect, sitting at top-end of the particle. (b) For a slightly longer microrod, the Saturn ring is stable also in the middle position. It has to be pushed with an optical trap (red cross) to transform back into a point defect. (c) The point defect can be further grabbed by an isotropic droplet, induced by the heating of high-power optical trap and an elongated defect is formed from the hedgehog to the isotropic island. (d) Using a medium trapping power, a Fréedericksz transition is induced locally in the nematic fluid, which is visible as a greyish circle above the microrod. The distorted region is used to grab the Saturn ring and to pull it away from the particle. Adapted from Tkalec *et al.* [35].

Topological properties of the director pattern can be revealed in greater detail by using the optical tweezers. It has been shown that topological defects in liquid crystals can be trapped and manipulated using the highly focused laser beam of optical tweezers [51,31,50,80,81]. Figure 5.3(a) shows an example where the point defect of the dipolar microrod, oriented along the director, is located in the middle of the rod. This was achieved by dragging the defect from its initial position at the end of the rod using an optical trap. During the procedure, the hyperbolic point defect has opened into the $-\frac{1}{2}$ defect line, encircling the microrod in the form of the Saturn ring. Such metastable position of the Saturn ring spontaneously transforms back to the point defect, as the stability of the Saturn ring primarily depends on the length of the rod. As illustrated in Fig. 5.3(b), such a ring is stable for a slightly longer microrod. Using optical trap, one can still grab and drag the ring to the stable position at the end of the particle. Figure 5.3(c, d) shows another two examples of defect manipulation, which help us to elucidate the shape and position of topological defects. In Fig. 5.3(c), the trapping power was increased to the extent, that the nematic phase was locally melted into the isotropic phase. The isotropic island is clearly visible because of the isotropic-nematic phase boundary due to the first order nature of the phase transition. Using this isotropic island as a seed, a point defect of a dipolar microrod has been grabbed and transformed by pulling into an elongated topological defect, connecting the isotropic island and the microrod. The second example in Fig. 5.3(d) shows that there is indeed a Saturn ring, encircling the quadrupolar microrod along its longer axis. This ring can be grabbed by the tweezers and pulled away from the microrod, confirming the evidence of predicted topological configuration.

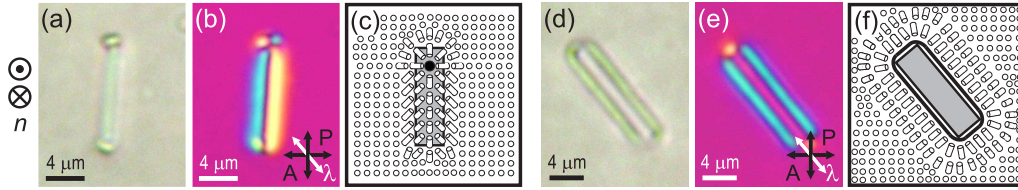


Figure 5.4: (a-c) Dipolar microrod in the homeotropic cell of 5CB. The location of the point defect is clearly visible on top of the microrod in (b). (d-f) The quadrupolar configuration is characterized by a $-\frac{1}{2}$ disclination loop, encircling the particle in the plane of the image. When a red plate is inserted, the differently colored regions of birefringent nematic indicate different orientations of liquid crystal molecules, which can be schematically illustrated. Reprinted from Tkalec *et al.* [35].

We have also analyzed the director pattern around homeotropic microrods in a cell, inducing the homeotropic alignment of 5CB, which is presented in Fig. 5.4. The dipolar configuration is shown in Fig. 5.4(a-c), and from the polarized optical micrograph it is evident that the hedgehog point defect is located close to the top-end of the particle. The presence of the Saturn ring around a quadrupolar microrod is also clearly evident from Fig. 5.4(d-f). Here, one can easily determine the local orientation of the molecules by using the red plate, as well as identifying the ring, which is clearly distinguished from depolarized image in Fig. 5.4(d).

5.1.2 Interactions between dipolar and quadrupolar microrods

The anisotropic interaction forces between two dipolar and quadrupolar microrods have been directly measured using the particle tracking video microscopy [207], combined with optical tweezing of particle pairs. Dissipative drag forces experienced by colloidal particles moving in nematic liquid crystal are known to be quite complex due to the intricate coupling of orientational order to the flow fields, induced by the particle motion, as well as the inherent anisotropy of shear viscosities of the liquid crystal [36,227]. Nevertheless, in the Stokes regime, the drag force on a microrod has been determined by performing another Brownian motion experiment, where the microrod experiences a random thermal motion. The observed fluctuations are highly anisotropic as the microrod experiences much more vivid motion along the director than in the

perpendicular direction. However, one can also notice that there was a latent flow of the solvent, as evidenced from the analysis of the sequent Brownian moves, presented in the distribution in Fig. 5.5(a). The x axis of the graph shows a displacement of the microrod during 300 ms long time intervals, while the y axis presents the number of steps out of the total 11000 steps recorded in the experiment. The distribution representing the motion parallel to the nematic director is displaced in the $+$ direction, which indicates macroscopic flow. The widths of both distributions allow us to determine diffusion coefficients for each direction (see Section 4.1.1). Finally, using the Stokes-Einstein relation we can estimate the product of the effective dimension and viscosity, which is in this case equal to $\gamma_{\parallel} = 0.8 \cdot 10^{-6}$ kg/s and $\gamma_{\perp} = 2.2 \cdot 10^{-6}$ kg/s, respectively.

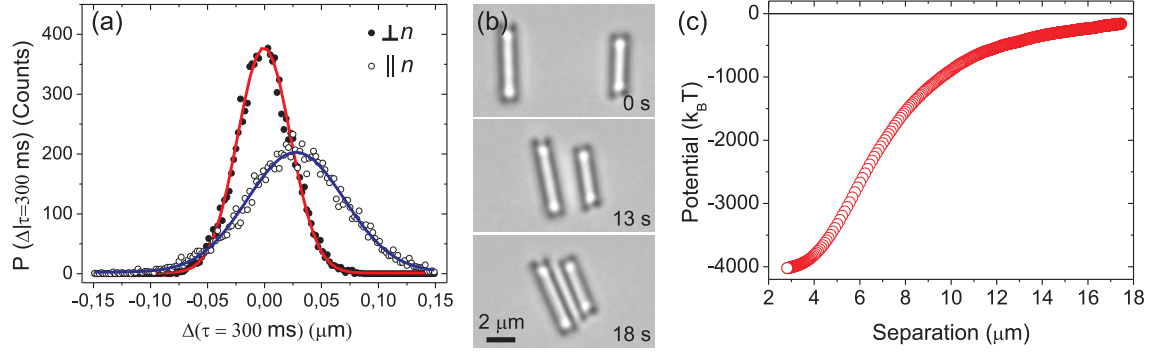


Figure 5.5: (a) Brownian motion of dipolar microrod in the nematic liquid crystal. Note the extreme anisotropy of the movement, which is partially caused by macroscopic flow of the solvent. For each 300 ms long time interval, the length of displacement is measured and plotted in a histogram. (b) Side-by-side attraction of a pair of microrods with the opposite direction of their topological dipoles. (c) Lateral attractive potential of antiparallel dipolar rod-like configurations. Adapted from Tkalec *et al.* [35].

Figure 5.5(b) presents a series of images, where side-by-side attraction of two antiparallel dipolar microrods has been recorded. The point defects are visible as tiny spots on the top side and the bottom side of the rods, respectively. The attraction of two dipolar microrods is therefore similar to the attraction of two electric dipoles with opposite directions. In equilibrium, they are tilted at a certain angle with respect to the rubbing direction, which is similar to what has been observed for dipolar chains of spherical particles [80]. The force and the pair potential as a function of separation were calculated from the recorded series of images (see Section 4.2.1). The results, shown in Fig. 5.5(c), explain that $1.5 \mu\text{m}$ diameter microrods attract each other more than $12 \mu\text{m}$ apart, and the depth of the potential well is close to $4000 k_B T$. As anticipated, these values are comparable to the pair interaction energy of dipolar chains of comparable size.

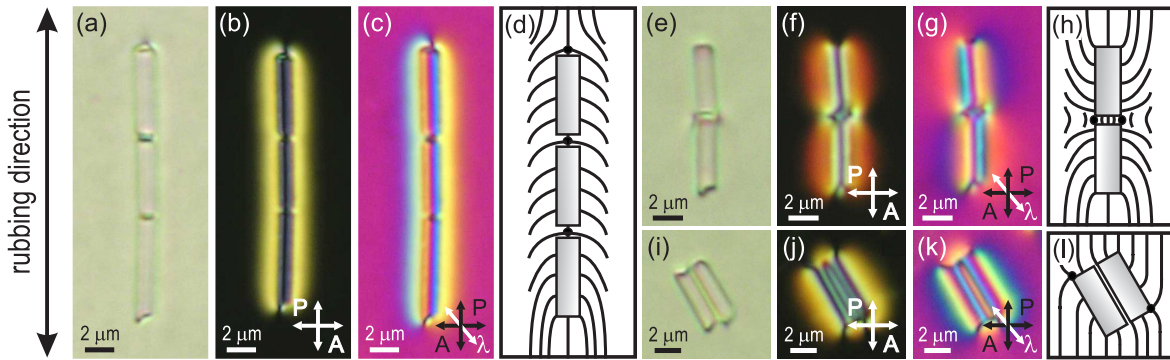


Figure 5.6: Stable pair configurations of dipolar microrods in a planar nematic cell. (a-d) Dipolar chain of microrods as observed under polarizing optical microscope. (e-h) Bubble-gum configuration of two antiparallel and collinear dipolar microrods. (i-l) Side-by-side configuration of two antiparallel dipolar microrods. Adapted from Tkalec *et al.* [35].

Similar to the interaction between dipolar microspheres in the nematic solvent, the dipolar microrods also attract collinearly with their topological dipoles directed in the same direction. Figure 5.6 presents a summary of stable pair configurations, assembled from dipolar microrods in a planar nematic cell, together with images taken between crossed polarizers with inserted red plate and schematic illustrations of the director field. The similarities with a nematic dispersion of microspheres are evident and help us to elucidate stable colloidal structures of quadrupolar microrods.

The interactions between quadrupolar microrods have been studied by positioning a pair of microrods at a predetermined position using optical tweezers and by subsequent following of their trajectories. The microrod pair interaction in a planar cell is quite similar to the interaction between spherical elastic quadrupoles [81]. The difference is that with microrods, there are two distinct equilibrium pair configurations: side-by-side and top-down configuration, shown in Fig. 5.7(a-d) and Fig. 5.7(e-h), respectively.

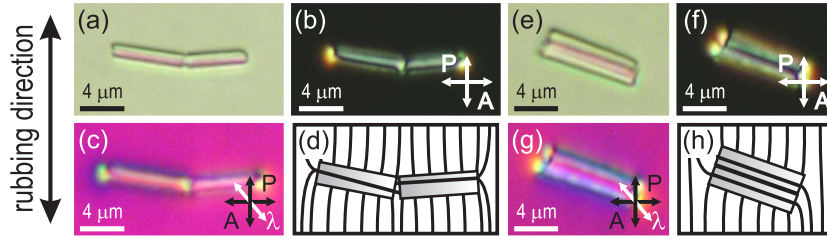


Figure 5.7: Stable pair configurations of quadrupolar microrods in a planar nematic cell. (a-d) Side-by-side and (e-h) top-down configuration of two quadrupolar microrods. Adapted from Tkalec *et al.* [35].

The overall similarities with spherical nematic dispersions are evident and help us to compare experimental results with several numerical calculations. It is important to note that the finite size of microrods matters, as it determines the location of topological defects. Our observations of the director field distortion around quadrupolar microrods, shown in Fig. 5.2(d-f), are in agreement with prediction of Hung *et al.* [253,254] that in equilibrium, the quadrupolar microrod with homeotropic boundary conditions has to be oriented perpendicularly to the far-field nematic director. They have also noticed that a $-\frac{1}{2}$ defect line encircles the microrod along its longer axis and announced that the same defect line could appear in a form of axially symmetric coat, spreading along the elongated particle. Hung *et al.* have also predicted that quadrupolar nanorods can form three stable pair configurations [253], which is in full agreement with our equilibrium pair configurations, shown in Fig. 5.7. Moreover, our experiments with quadrupolar microrods in thicker nematic cells indicate that particle pairs could be formed also in a way where one microrod slips on the top of the other. This opens a real possibility of forming three-dimensional (3D) periodic structures of elongated particles in nematic liquid crystal. The crucial parameter to achieve this goal, unfortunately hardly assured in glass microrod production, is the uniform length and well-defined edges of individual particles.

The recent experimental results from Lapointe *et al.* [36] have shown that elastic colloidal interactions in anisotropic fluids are sensitive to the particles' shapes. Equilibrium director field configurations around equilateral polygonal colloids exhibit either dipolar or quadrupolar symmetries, depending on whether their number of sides is odd or even. The generated inter-particle forces among such polygonal platelets drive the highly directional assembly of a number of ensuing self-assembled colloidal architectures. Another recent results of Mondiot *et al.* [259] have shown that micrometer-sized ellipsoidal particles with planar surface anchoring of nematic liquid crystal exhibit a transition from an aggregated to a non-aggregated state, which is a function of aspect ratio at a given particle concentration. Together with boundary conditions, the particle shape may therefore be exploited to tune interactions among non-spherical inclusions in liquid crystal solvents. These exciting results show that the exploration of anisotropic nematic colloids has begun and we can expect a splendid variety of new structures in the near future.

5.2 Vortex-like defect rings in chiral nematic colloids

We show that chiral ordering of the underlying anisotropic fluid influences defect formation and colloidal interactions in confined geometry of a twisted nematic cell. The induced chirality builds a spatially dependent director and stabilizes escaped vortex-like defect loops. These loops are binding spontaneously formed pairs of colloidal particles, named dimers, that are chiral objects. Interparticle interaction weakly depends on the chirality of dimers and leads to the assembly of novel two-dimensional nematic colloidal crystals of pure or mixed chirality. These regular structures are thermodynamically stabilized by the intercalation of non-singular defect rings. Moreover, we affirm that escaped defect structures are closely related to entangled defect configurations in chiral nematic medium and demonstrate how they can be reversibly transformed one to another.

5.2.1 Escaped hyperbolic defect rings and colloidal dimers

Bubble-gum configuration with escaped hyperbolic defect ring, introduced in Chapter 4, is highly metastable with respect to elastic dipoles and quadrupoles in the geometry of an uniform planar nematic cell [131,136,233]. However, its intrinsically induced deformation of the director field rises a question, whether the stability and metastability of the bubble-gum configuration could be reversed by using external fields or more appropriate cell geometry with a non-uniform director.

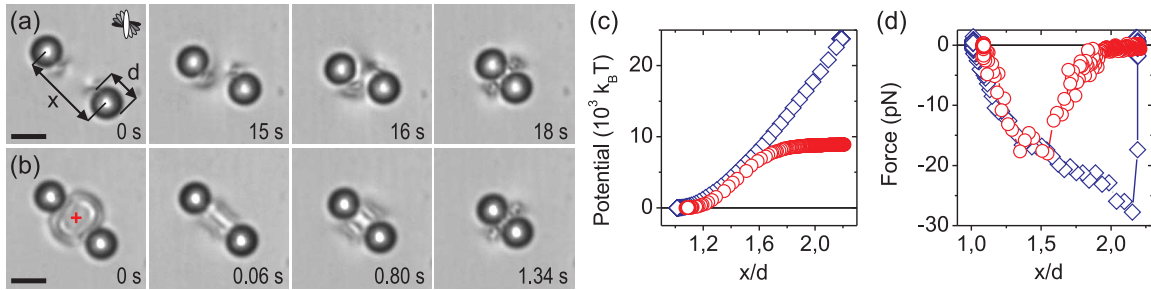


Figure 5.8: (a) In 90° twisted nematic cell two antiparallel dipoles spontaneously fuse into a dimer, sharing a single escaped defect ring. (b) An isotropic droplet, induced by the optical trap, melts the intermediate region and separates the particles. After switching-off the light, the particles are attracted by two thin birefringent strings, characteristic of the escaped non-singular ring disclination. Note the difference between final states in (a) and (b). (c) Separation dependence of the attractive potential, determined from (a) (red circles) and (b) (blue squares). (d) Corresponding forces are roughly independent of particle separation. Scale bars correspond to $5 \mu\text{m}$ and the cell thickness corresponds to $8 \mu\text{m}$.

Experiments were performed in 90° twisted nematic cell with perpendicular top and bottom surface orientation. Inside the cell either left or right-twisted nematic domains are established, depending on the direction of the twist. Colloidal structures built in a given twist domain are equivalent to structures in the opposite domain. Spontaneous formation of colloidal dimers is immediately observed in the left-twisted nematic domain, as illustrated in Fig. 5.8(a). Here, two antiparallel dipolar colloidal particles are oriented at 45° with respect to both rubbing directions and are attracted to each other along the shortest path. After spontaneous 'fusion' a new defect ring is formed between the colloids. We disturb it by using the local heating of laser light, which creates a small droplet of the isotropic phase, holding the particles apart [Fig. 5.8(b)]. After switching-off the light two thin birefringent strings are created and they pull both particles together. These strings are characteristic of the escaped non-singular ring disclination, which must have been created from two singular hyperbolic point defects [136,233].

Class of escaped non-singular topological defects in a nematic fluid was first experimentally observed and theoretically studied by Patricia Cladis and Maurice Kleman [132,134]. The energy, stored in a singular point defect, confined within capillary tube with perpendicular boundary conditions, has been released by escaping of the molecular ordering into the third dimension, thus strongly reducing the spatial variations of the nematic order. Many years later, Robert

Meyer proposed the director field escape mechanism in a nematic colloidal dispersion [131], where two hyperbolic point defects, belonging to the antiparallel elastic dipoles, transformed into escaped non-singular disclination ring, binding two particles into inseparable pair with a string-like potential. Topologically, such disclination ring is equivalent to the point defect and carries a topological charge of -2 with a -1 local strength of the line. Structures, bound by escaped defect rings, are rarely observed in planar nematic cells due to their complex and highly energetic structure when compared to antiparallel elastic dipoles [233]. Opposite to that, the binding energy of escaped defect ring in 90° twisted nematic cell exceeds $10000 k_B T$, which means substantially stronger binding than $7500 k_B T$ in the case of antiparallel dipoles. Therefore, colloidal pairs bound by non-singular defect loops are energetically more favorable in chiral nematic host, which is evidently reflected in the high probability of their spontaneous formation. The chiral ordering of the liquid crystal thus profoundly alters the nature and stability of topological defects. Instead of singular point defects, which are characteristic for homogeneous nematic fluids, chirality proliferates non-singular defects in the form of twisted torus with a cross-section that is identical to magnetic hyperbolic vortices [260]. In this respect, the effective chiral interaction in liquid crystal is analogous to the Dzyaloshinskii-Moriya spin-orbit interaction [261], which generates skyrmion ground states in magnetic systems [166,262].

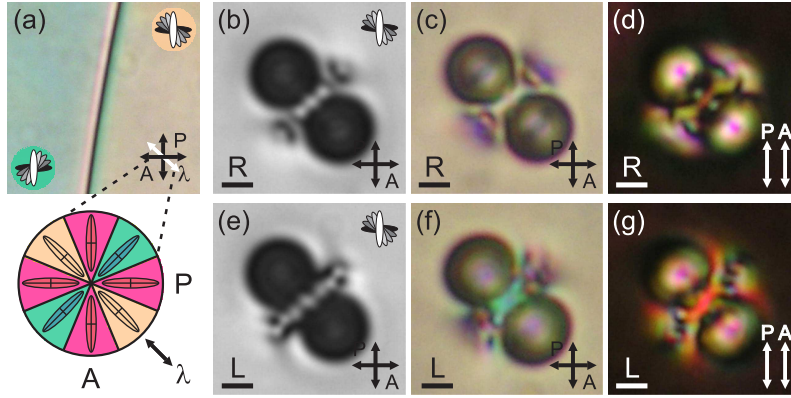


Figure 5.9: Two colloidal dimers of the opposite chirality coexist in left-twisted nematic domain. (a) The handedness of nematic domain is clearly distinguished between crossed polarizers with inserted red plate λ , when different twists appear in different colors. Energetically preferable right-handed dimer (R) between crossed (b, c) and parallel polarizers (d). Left-handed dimer (L) between crossed (e, f) and parallel polarizers (g). Left-handed twist is indicated in (b) and (e). Birefringence colors shown different orientations of nematic molecules. Scale bars correspond to $2 \mu\text{m}$. Adapted from Tkalec *et al.* [97].

When the defect ring is perturbed by dragging the optical trap along it, another colloidal dimer, which is quite similar to the first, could be created. However, these two colloidal dimers are clearly different, as can be noticed already in Fig. 5.8. By comparing the fine structure and birefringence colors of the defects in Fig. 5.9, one can claim that first configuration, shown in Fig. 5.9(b-d), is clearly different from the second one, shown in Fig. 5.9(e-g). The difference is in the chirality of colloidal dimers, which is due to the mechanism of director escape, illustrated in Fig. 5.10. In contrast to the case of a radial $+1$ defect line, that escapes either up or down (or down and up) in two perpendicular planes, as presented in Fig. 5.10(b, c). The singularity of the director field in the center of the -1 defect line disappears and a non-singular escaped director field with only minor variations of the nematic degree of order is established. Such escape into the third dimension reduces the strong elastic deformation within the defect core and it also lowers the total elastic free energy. By connecting the escaped defect line into a loop, a chiral object with a given handedness is generated. The handedness of the escaped defect ring is invariant with respect to rotations but changes with a mirror transformation, as indicated in Fig. 5.10(d). Topologically, such escaped defect ring is homotopic to a point defect with

topological charge of magnitude 2. In planar nematic cell, escaped hyperbolic defect rings of the opposite handedness are inherently indistinguishable, whereas the twisted nematic host removes the degeneracy. In contrast to the recent prediction by Fukuda *et al.* [233], distinguishable particles are not necessary required to obtain the difference in the escape direction.

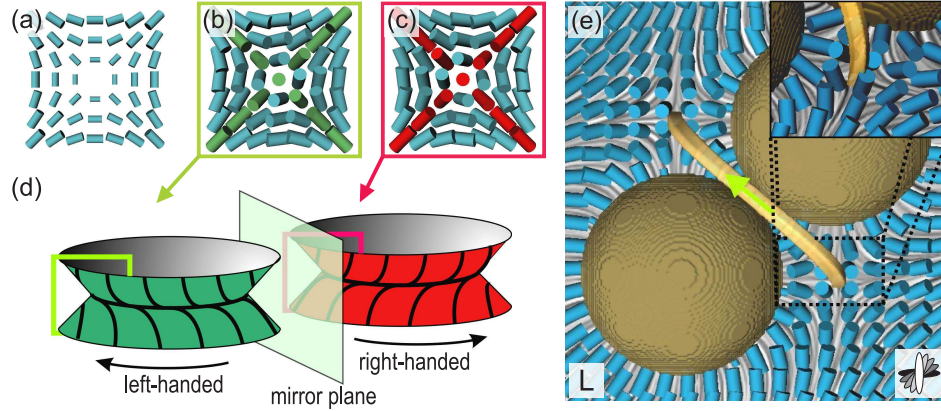


Figure 5.10: Director escape mechanism. (a) Cross section of a singular hyperbolic defect line, which escapes simultaneously either up-down or down-up in two perpendicular planes, as indicated in (b) green and (c) red, respectively. (d) Connecting the escaped hyperbolic defect lines into loops, two escaped hyperbolic defect rings with the opposite handedness are generated. (e) Escaped colloidal dimer, calculated from LdG theory. Arrow indicates the handedness of the ring. Adapted from Tkalec *et al.* [97].

In equilibrium the escaped defect rings are slightly deformed to minimize the elastic distortion. The handedness of the escaped defect ring affects both the nematic profile and the energetic stability of two opposite-handed colloidal dimers. In particular at its top and bottom, the escaped defect ring induces rather different distortions in the surrounding nematic, depending on the handedness of the ring and the handedness of the bulk nematic twist. This causes a significant difference in the total free energies of the studied configurations. Numerical calculations have shown that the opposite handedness of the liquid crystal twist and the escaped hyperbolic defect ring result in 15 % reduction of the binding energy compared to the equal handedness of both [97]. The fine structure of energetically preferable colloidal dimer is shown in Fig. 5.10(e).

Only recently it has been shown by Smalyukh *et al.* [263] that robust multi-stable optical switching of twisted particle-like excitations in anisotropic fluids can be performed by focusing Laguerre-Gaussian vortex beams. These toron structures with topological charge of magnitude 2, owing to the twist-escaped disclination ring, are closely related to our escaped hyperbolic defect rings that intercalate colloidal particles, yet they can be stabilized without colloids due to a different liquid crystal cell geometry.

5.2.2 Two-dimensional nematic colloidal crystals based on escaped hyperbolic defect rings

To our surprise, the director escape mechanism leads also to strong attraction between colloidal dimers and even to formation of multi-particle clusters, chains and novel 2D colloidal crystals. The interaction was analyzed using the optical manipulation of selected chiral colloidal dimer to a predetermined position with respect to the other [Fig. 5.11(a)]. After being released, trajectories are clearly attractive from any of the starting positions 1 – 12 and the dimers are neatly packed into square 2D lattice in a short time [Fig. 5.11(b)]. The strength and the range of the attractive potential, presented in Fig. 5.11(c), were measured by video microscopy and particle tracking routines (see Chapter 3). The interaction is strongly attractive, namely of the order of $5000 k_B T$ per $10 \mu\text{m}$ big dimer. It is roughly independent of the chirality of colloidal dimers, allowing for the 2D colloidal crystals with mixed building dimer blocks to be assembled as well.

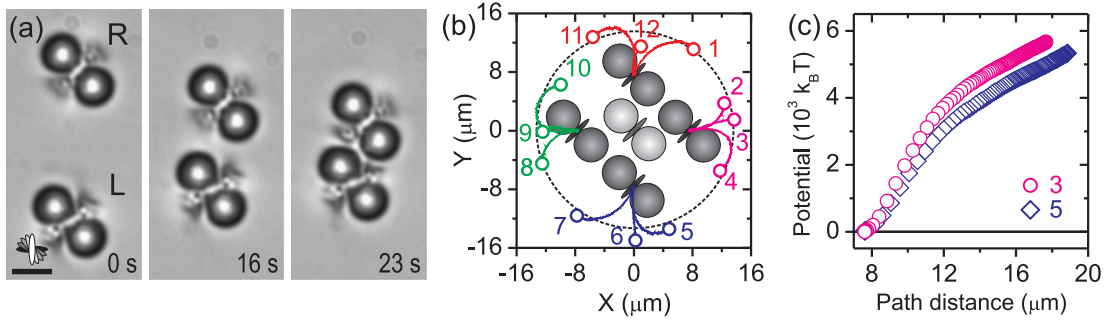


Figure 5.11: (a) Attractive interaction between two colloidal dimers of the oppositely-escaped defect rings. (b) Anisotropy of attraction between right-handed colloidal dimers in the left-twisted nematic domain. Starting positions are labeled 1 – 12 and interaction trajectories are drawn. (c) Separation dependence of the attractive potential between two colloidal dimers of the same chirality, determined from trajectories, starting from positions 3 and 5, presented in (b). Scale bar corresponds to 5 μm and the cell thickness corresponds to 8 μm . Adapted from Tkalec *et al.* [97].

Figure 5.12 shows three different 2D nematic colloidal crystals, assembled from chiral colloidal dimers. A crystal assembled from right-handed (*R*) colloidal dimers in a left-twisted nematic domain is shown in Fig. 5.12(a, d). The unit cell is square with lattice constants: $a = 7.93 \pm 0.07 \mu\text{m}$, $b = 5.02 \pm 0.07 \mu\text{m}$, $\phi = 45^\circ \pm 1^\circ$. The crystal from left-handed (*L*) dimers in a left-twisted nematic domain is shown in Fig. 5.12(b, e). The unit cell is also square with basis: $a = 7.57 \pm 0.07 \mu\text{m}$, $b = 4.92 \pm 0.07 \mu\text{m}$, $\phi = 45^\circ \pm 1^\circ$. The right-handed colloidal crystal is, similar to particle dimers, energetically more stable than left-handed crystal in the left-twisted nematic domain, having $\sim 15\%$ lower total free energy [97]. Energetically more favorable coupling of the external twist with the right-handed escaped defect rings also allows larger unit cell size. Figure 5.12(c, f) shows a 'mixed' 2D crystal, where an equal number of left and right-handed colloidal dimers were used.

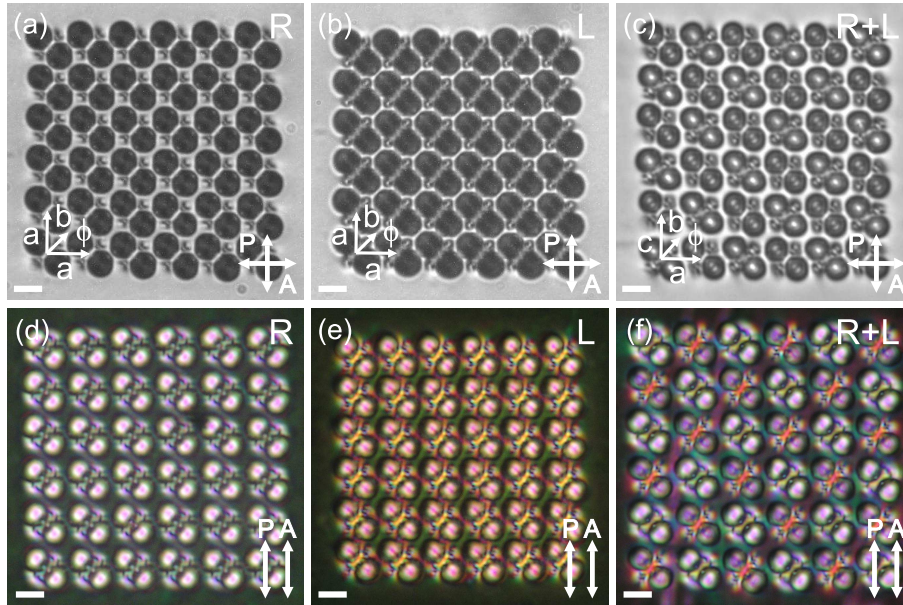


Figure 5.12: 2D nematic colloidal crystals assembled from chiral colloidal dimers using optical tweezers. Crystal lattice, made of right-handed dimers in left-twisted nematic domain between (a) crossed and (d) parallel polarizers. Crystal lattice, made of left-handed dimers in left-twisted nematic domain between (b) crossed and (e) parallel polarizers. 2D mixed nematic colloidal crystal, assembled from equal number of left and right-handed dimers between (c) crossed and (f) parallel polarizers. Note the difference between opposite-handed escaped defect rings. Scale bars correspond to 5 μm . Reprinted from Tkalec *et al.* [97].

Since square symmetry of the crystalline lattice requires either an interaction with a fourfold symmetry axis or a very particular separation dependence of interaction, it is not a very common structure [264]. Here, it originates from the local symmetry of the -1 hyperbolic defect rings. Ignoring first, the external twist imposed by the cell substrates and escape of the defect rings, locally, the director surrounding the defect ring has 90° rotational symmetry. Any deviation of the director from this symmetry is energetically strongly penalized, which together with preferred homeotropic alignment at particle surface favors only distinct directions for assembly of neighboring particles. The director regions that point radially from the center of a particular escaped ring build two perpendicular straight lines. Consequently, they are energetically in favor of coupling to homeotropic surfaces of neighboring dimers in case the neighboring particles are positioned exactly along these lines [97]. Together with crystalline symmetry this results in a square unit cell. The situation is different in quadrupolar nematic colloidal crystals with $-\frac{1}{2}$ defect rings, where director has locally 120° rotational symmetry, which results in a roughly hexagonal colloidal lattice [31]. Accounting for the external twist and escape of the defect rings, they violate the leading square symmetry, giving rise to the small asymmetry in lattice constants.

5.2.3 Topological transformations of escaped hyperbolic defect rings

Using optical tweezers we have observed that escaped hyperbolic defect ring with a topological charge of -2 is created due to the fusion of two -1 hyperbolic point defects, accompanying antiparallel elastic dipoles. It is important to note that a singular disclination line cannot escape to a third dimension unless its topological charge is an integer. Therefore a single defect ring with $-\frac{1}{2}$ topological charge cannot be converted to a non-singular configuration. Only when two $-\frac{1}{2}$ defect rings are combined together, a non-singular configuration can be realized [233]. This fact clearly demonstrates that the orientational configuration around two or more colloidal particles can be far richer than just a superposition of the orientation profiles of individual particles and that various transformations among different classes of topological defects are possible.

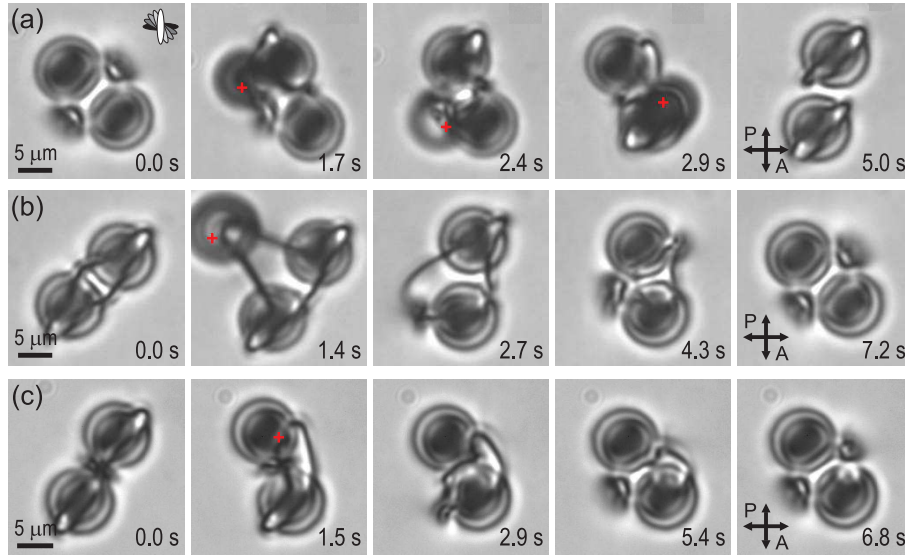


Figure 5.13: Topological transformation of the escaped hyperbolic defect ring due to the change of relative particle positions. (a) Chiral colloidal dimer transforms to a pair of elastic quadrupoles after a melting of the defect core. (b) Figure of eight defect configuration is easily transformed to the non-singular defect ring. Initially, the defect line locally unwinds and transforms into two separated point defects and then the point defects are fused together into escaped defect ring of double topological charge. (c) Similarly, the entangled point defect is transformed into the chiral colloidal dimer. Here only one point defect is formed out of the entangled defect line, while the other one is already present in between the colloidal particles. A low-power optical trap is indicated by the red cross.

Firstly, in Fig. 5.13(a), we show the topological transformation of escaped hyperbolic defect ring into two separate Saturn rings in the left-twisted nematic domain. Applying the optical trap, we initially grab the non-singular defect ring and pull it away from the particles. Immediately, a source of a $-\frac{1}{2}$ disclination line is formed around the upper particle and when the escaped defect core is melted completely, also the lower particle is surrounded by the Saturn ring. Individually, each Saturn ring makes a tie in the shape of the figure of eight, if looked from above. After the transformation, in order to minimize the elastic deformation imposed by the external twist, the quadrupolar pair is rotated, forming the 90° angle with respect to initial configuration. In twisted nematic cell the quadrupolar pair is metastable and easily transformable to the entangled figure of eight configuration. Interestingly, it is even not necessary to perform a temperature quench in order to generate the entangled structure because its equilibrium coupling to the equally-handed external twist results in the minimal elastic deformation [222]. Furthermore, the figure of eight can be smoothly transformed back to escaped hyperbolic ring only by changing the relative position of the particles, as shown in Fig. 5.13(b). The $-\frac{1}{2}$ defect line firstly unwinds and consequently collapses into two slightly separated -1 hyperbolic point defects, which rapidly join into escaped defect ring. Similarly, the entangled point defect is transformed to the vortex-like defect configuration. Here, the $-\frac{1}{2}$ defect line unwinds only on one side of the colloidal pair in order to produce a single -1 hyperbolic point defect, while the second -1 point defect is already present in between the particles, as clearly evidenced from Fig. 5.13(c). These examples clearly demonstrate how singular and non-singular topological defects can be transformed among each other in the presence of colloidal particles.

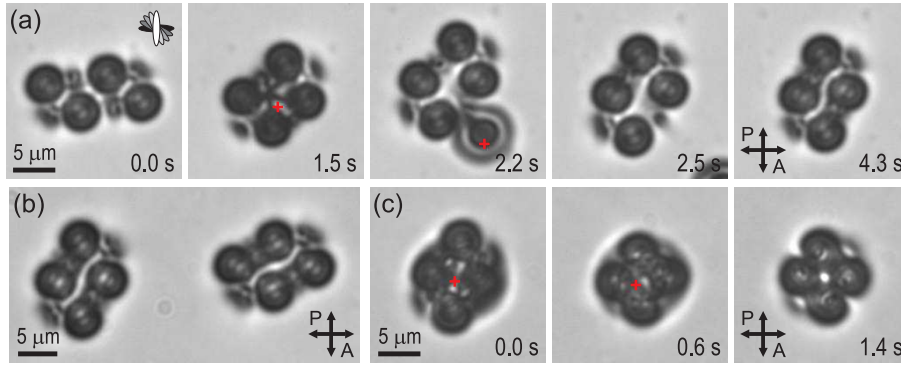


Figure 5.14: (a) Laser-induced optical fusion of initially separated escaped hyperbolic defect rings into tetramer cluster. (b) Two equilibrium orientations of tetramer cluster have been observed. (c) Clover-shaped colloidal cluster with highly twisted director field can be finally created from tetramer cluster.

Escaped hyperbolic defect rings are not limited only to colloidal dimers but they can expand over larger colloidal clusters. Figure 5.14 shows laser-induced optical fusion of initially separated chiral dimers of the same handedness into a tetramer cluster. Such cluster has two equivalent equilibrium orientations that can be easily switched and further assembled into pairs or chains of extended non-singular disclination. Moreover, the colloidal tetramer is further transformed to the clover-shaped cluster, where particles, connected with highly twisted non-singular defect loop, occupy positions in two different planes. The exact director field configuration of similar structures is highly likely to be of interest in the future studies.

An analogy can be found between colloids bound by entangled and escaped defect structures. In both configurations the defects stabilize topologically inseparable objects and they can be considered as new building blocks for larger colloidal structures. In both cases complex defect loops have a topological charge larger than 1 and therefore due to energetic restrictions can not exist in a bulk nematic unless together with particles. Finally, both defect configurations are characterized by a string-like potential, suggesting that the elastic deformation is a linear function of the particle separation.

5.3 Knots and links in chiral nematic colloids

In this Section the most exciting results of the thesis are presented, showing that knots and links of various complexity can be achieved and arbitrary reconfigured on a microscopic scale by optical manipulation in confined chiral nematic colloidal dispersion. The objects that possess topological structure of knots and links are stable defect lines in the molecular orientation field of liquid crystal. We have performed a systematic study of diverse defect entanglements by using methods of mathematical theory of knots and have demonstrated that by applying local transformations of basic constituents one can reconfigure topological conformations in a controlled manner and determine their inter-related recurrence. Many non-trivial conformations belong to the family of torus knots and links, but alternating achiral knots and multi-component links have been identified as well. Furthermore, by orienting the defect loops arrested in between the confining surfaces, we have created an effective record of topological structures, encoded in the periodic sequence of letters. Then, by using selective optical trapping we have been able to perform site-specific recombination of defect segments and to identify every structural transition between adjacent topological conformations. Surprisingly, all structural transitions are based on two specific modifications of oriented defect strands, called inversion and exchange, which are otherwise performed on molecular level by recombination enzymes that manipulate DNA molecules during the replication and genetic recombination. Knots and links, made from topological defects in anisotropic fluids, are relatively easy to design and they can assume a variety of structural motifs with different topological properties. These can find applications as a model system for the study of knotted conformations in confined and chiral environment, as well as light-addressed optical switches, bistable nematic liquid crystal device or as topological target for the scaffolding of dispersed biopolymers and nanoparticles.

5.3.1 How to weave nematic braids?

In Chapter 4 it has been shown that entangled colloidal structures bound by delocalized defect loops are metastable with respect to the non-entangled structures of elastic dipoles and quadrupoles in the geometry of an uniform director field. The entangled conformations are accessed exclusively through the local temperature quench from the isotropic to the nematic phase. However, their asymmetry and intrinsically induced deformation of the director field rise a question whether by using external fields or more appropriate cell geometry with a non-uniform director, the entanglement phenomena could be generalized to 2D assemblies of micrometer-sized colloidal particles.

As already indicated in Section 5.2, the twisted nematic cell builds a spatially varying director field, which highly stabilizes entangled colloidal structures. In experiments presented here, a dispersion of $4.72\ \mu\text{m}$ diameter silica spheres in 5CB nematic liquid crystal was introduced into $6\ \mu\text{m}$ thick 90° twisted nematic cell. The particle surfaces were treated chemically to induce perpendicular surface orientation of the liquid crystalline molecules and the confining substrates were rubbed mechanically to induce planar molecular alignment along the rubbing direction (for details see Section 3.1.2). Top and bottom surface orientations were set perpendicularly to each other, therefore the helical winding of nematic molecules was either left or right-handed, depending on direction of the twist. Colloidal structures in a given twist domain are equivalent to structures in the opposite-twisted domain, so we have focused on the left-twisted domain unless otherwise stated. As the thickness of the twisted nematic cell is only slightly larger than the diameter of the particle, the geometrical frustration of the director field around the spherical inclusion adopts a quadrupolar symmetry [21]. Consequently, topological defect in the form of a twisted Saturn ring is spontaneously formed, encircling the colloidal particle in the shape of the figure of eight, if looked from above. The defect ring lies in a plane, tilted at 45° with respect to both rubbing directions, and can be easily recognized in optical micrographs of Fig. 5.15.

The formation of spontaneously entangled structures has already been observed during the filling of the cell with nematic dispersion. Figure 5.15(a) shows a sequence of images, where a quadrupolar pair, entrapped into small region between neighboring entangled colloidal chains, is spontaneously transformed to energetically more favorable figure of eight configuration. The

binding force and the interaction potential, measured by stretching the entangled defect loop using optical tweezers, are highly robust and extremely strong, as shown in Fig. 5.15(d, e). Interestingly, it is even not necessary to perform a temperature quench in order to generate the entangled structure, but a suitable particle arrangement close to the equilibrium positions and external triggering of the liquid crystal flow are sufficient. Several simply entangled colloidal structures, assembled spontaneously during the material flow, are presented in Fig. 5.15(b). One can distinguish between twisted Saturn ring, figure of eight chain and entangled colloidal cluster, which has never been observed in spatially homogeneous nematic layers. The entangled cluster clearly demonstrates that the complexity of mesoscopic orientational ordering of the liquid crystal has substantially increased in spatially dependent director field. When the particle concentration is high and the macroscopic flow of the solvent is stopped, numerous entangled colloidal chains can be nicely observed between crossed polarizers. Now, defect lines appear completely visible and a detailed examination of Fig. 5.15(c) enlightens the spatial organization of entangled loops. One can notice that each colloidal particle supports a crossing of two perpendicularly oriented defect strands in two different planes. These crossings are imprints of twisted Saturn rings, where one defect strand of a certain direction lies above the particle and then continues in another strand which sinks below the particle that is oriented perpendicularly to the first strand. The imposed orientational ordering of defect strands is defined by the boundary conditions at confining surfaces.

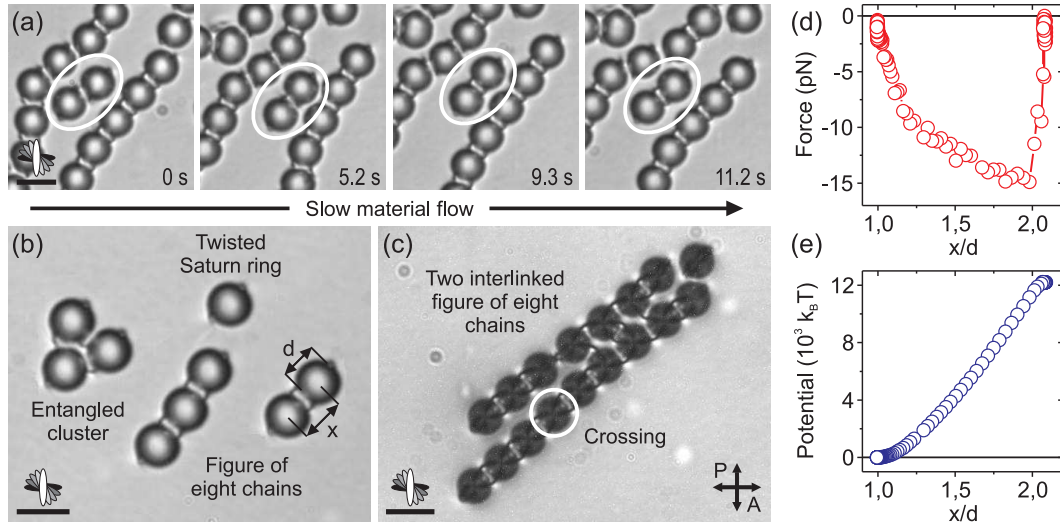


Figure 5.15: Spontaneously entangled colloidal structures in a twisted nematic cell. (a) Twisted defect ring appears spontaneously around individual spherical particle with homeotropic surface anchoring in the geometry of left-twisted nematic domain, as viewed from above. These rings readily join into figure of eight pairs (see white encircled region) or entangled chains during the flow of nematic dispersion. (b) Collection of spontaneously entangled colloidal structures, including figure of eight chain and a small entangled cluster. (c) Surprisingly, even the lateral entanglement of figure of eight chains is energetically favorable. (d) The effective structural force and (e) the interparticle potential for the figure of eight demonstrate extremely strong binding of entangled defect loop. Scale bars correspond to $5\ \mu\text{m}$.

In order to understand the observed colloidal structures, we have focused on the controlled fusion of separated defect loops using optical tweezers. Examples of creation and manipulation of small entangled colloidal clusters are shown in Fig. 5.16. We have used low-power optical trap ($\approx 30\ \text{mW}$) to manipulate particles inside the liquid crystalline matrix, while high-power laser beam ($\approx 60\ \text{mW}$) was used to perform a temperature quench of nematic volume in very localized region close to the particles. Since the entanglement of defect lines through the fast temperature quench is a stochastic process, we have repeated the quench several times in cases when the desired configuration was not obtained immediately. Initially, two separated twisted

Saturn rings were positioned close to each other and connected into the figure of eight using an optical trap [see Fig. 5.16(a)]. First of all, the optical trap was used as optical scissors, which cut defect strands by heating the nearby nematic fluid and then the same trap operated as an optical solder, which can rejoin the cut up strands due to the controlled cooling of the heated nematic region. Further, a new defect ring was attached to the figure of eight and consequently, an entangled colloidal trimer was formed. The fourth colloidal particle can be attached to entangled trimer at several different positions. We have attached it symmetrically to the previously attached particle and the formed cluster gained rhomboidal shape with two stable equilibrium orientations, presented in Fig. 5.16(c). Nevertheless, it can be considered as a superposition of two neighboring figure of eight structures, which clearly demonstrates that the entanglement of defect lines in two perpendicular directions is possible. The encircled tetramer can be further transformed into the crossed tetramer cluster due to the simultaneous melting of two lateral defect strands. After performed temperature quench the cut up strands are pairwise reconnected with the opposite strands, forming a crossing point in the middle of the colloidal structure. The obtained configuration is likewise entangled by a single defect loop, winding in another perpendicular direction around four colloids, as indicated in the last image of Fig. 5.16(d).

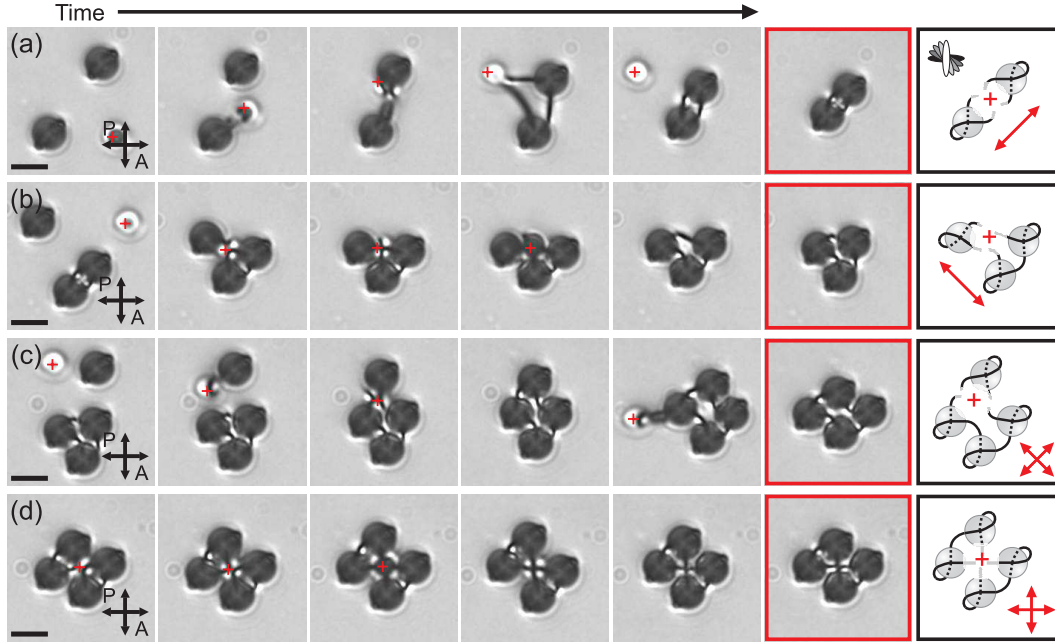


Figure 5.16: Creation and manipulation of small entangled colloidal clusters using optical trapping of defect strands. (a) Two separated microspheres with encircled Saturn rings are positioned close to each other and entangled by a single defect loop. The handles of both Saturn rings have to be cut by the laser light and afterwards rejoined in a figure of eight configuration. (b) The third particle is attached to the figure of eight, forming a tight elastic bond, shared among three colloids. (c) When the fourth defect ring is attached to the entangled trimer, several tetramer configurations are possible. In the first example, the defect line merges four particles into encircled cluster. (d) The encircled tetramer can be further transformed into the crossed tetramer by creating an inter-colloidal crossing of defect strands among the facing particles. Schematic illustrations show the regions, where an optical trap cuts and rejoins the defect strands, creating longer defect loops. Red arrows indicate four possible directions of a defect strand proliferation in 2D entangled colloidal clusters. Scale bars correspond to $5 \mu\text{m}$.

A collection of 2D entangled colloidal structures with up to four particles is presented in Fig. 5.17. The lower panels show corresponding equilibrium configurations, calculated numerically by free energy minimization technique that is based on phenomenological Landau-de Gennes model [8,222]. These simulations have been performed by M. Ravnik. The combination

of experimental and numerical results offers a more detailed insight into assembled structures and helps to elucidate topological properties of interwind defect loops. We have found that in terms of topology the entangled defect configurations in Fig. 5.17(a-e) are equivalent to the unknot, as they can be simply unwind in a single loop without any crossings. Moreover, in 2D entangled structures, presented in Fig. 5.17(c-e), each colloidal particle has a single handle of the remanent Saturn ring and shares two defect strands with exactly two neighboring particles. The handles change the direction of the winding defect lines and lift them from the bottom to the top (or vice versa) of the particles. However, the first non-trivial topological configuration is identified in another tetramer configuration, shown in Fig. 5.17(f). It is composed of two interlinked defect loops, which are equivalent to the Hopf link or catenane [151]. Here, two distinct colloids have no Saturn ring handles and they are connected to all remaining particles with four defect strands. This indicates that particular orientational ordering of defect strands might effectively change the number of defect loops, as well as topological properties of entangled objects.

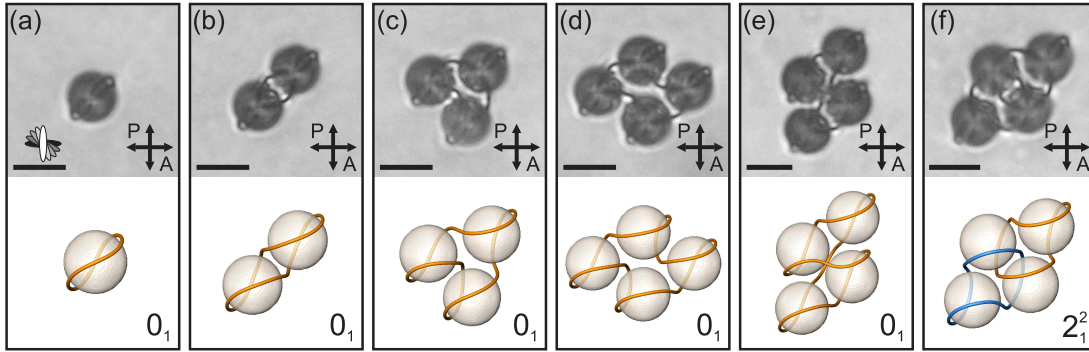


Figure 5.17: Collection of small entangled colloidal clusters. (a) Saturn ring appears spontaneously around homeotropic spherical particle and forms a tie in the shape of figure of eight, if observed from above. The ring generates a negative crossing in a left-twisted nematic domain and it is topologically equivalent to the unknot (see Section 2.7.2). (b) Figure of eight configuration entangles two microspheres in the form of double helix. (c) Entangled colloidal trimer, stabilized by the helical winding of a single defect loop, is the simplest 2D entangled colloidal configuration. (d) Entangled colloidal tetramer merges laterally two figure of eight configurations. (e) Crossed colloidal tetramer splits the encircled nematic domain into four pieces. One defect strand is running straight, while the other is bending in the form of Ω letter, as results from the numerical simulations. (f) Hopf link configuration, supporting two interlinked defect loops, is the first non-trivial topological conformation with the lowest number of particles observed. All numerical calculations have been performed by M. Ravnik. Traditional Rolfsen knot type notation is adopted [174]. Scale bars correspond to $5 \mu\text{m}$.

Trying to generalize the observed entangled clusters, the complex defect structures can be interpreted piecewise as combinations of entangled defect line configurations observed in entangled pairs. Defect lines between the neighboring particles are namely positioned, twisted and bent in a typical pattern, characteristic for the figure of eight and figure of omega configurations. Such behavior indicates that only specific configurations of defect lines are able to compensate the distortion imposed by spherical particles. Topologically, this implies that topological charge imposed by the particles can be compensated locally only by very specific arrangements of defect line segments, which could therefore be considered as carrying effectively opposite topological charge [85,121]. This information has to be valid when building 2D entangled colloidal structures.

5.3.2 How to knot defect lines?

Having observed differently entangled colloidal clusters, we have become interested whether more complex defect entanglements can arise when the number of linked colloidal particles is increased. Since it is known and intuitively expected that random entanglement of filaments in various physical systems increases with its length and/or density [265], we have attempted to

quantify the entanglement complexity of topological defect loops also in our system. In order to carry out this systematically, we have focused on periodical arrays of particles, organized into well-defined $p \times q$ colloidal templates. Here, p corresponds to the number of laterally positioned colloidal rows and q represents the number of particles along the individual row, as indicated in Fig. 5.18(a). Starting with six colloidal particles, we have initially created a topological isomer of the Hopf link, which closely resembles the previously entangled configuration in Fig. 5.17(f). The only difference is in two additional particles, which have been attached to the corners of the previous structure. Although the defect loops in both structures possess topologically equivalent conformation [compare Fig. 5.17(f) and Fig. 5.18(a)], they carry different topological charge, which elegantly removes the topological degeneracy (see Section 4.3.3). Topological charge of each loop in Fig. 5.17(f) equals 2, whereas in Fig. 5.18(a), it is equal to 3. This indicates that colloidal particles with remaining Saturn ring handle can not change the topology of entangled loops, but they effectively raise the total topological charge of entangled colloidal structures.

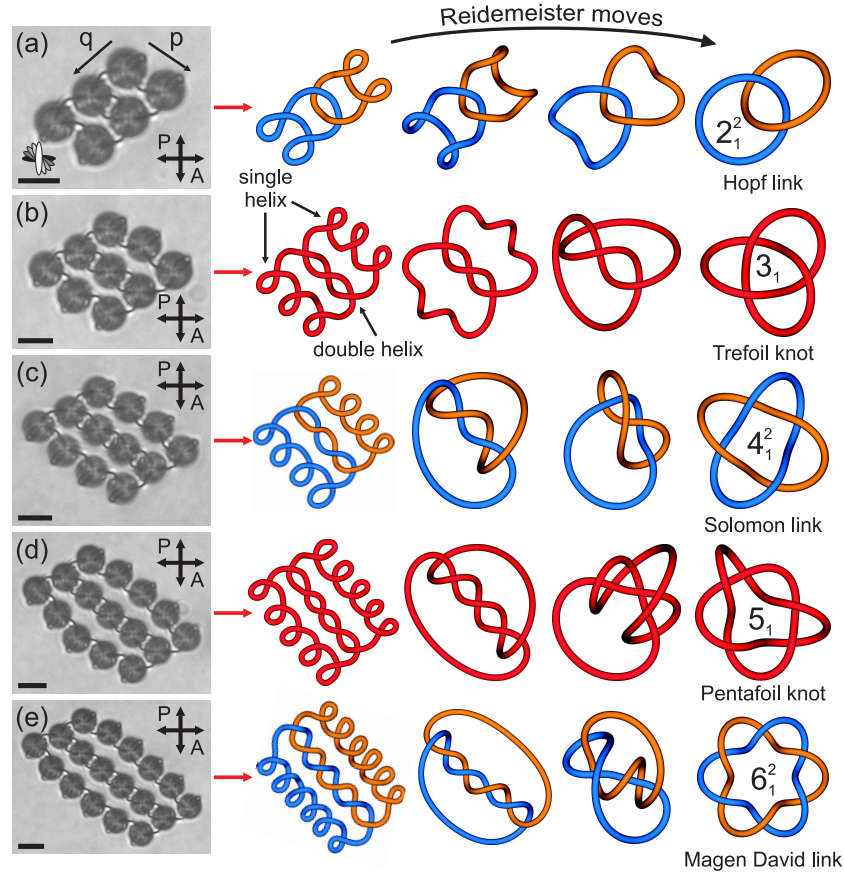


Figure 5.18: (a-e) Series of prime alternating torus knots and links are realized on generically similar $p \times 3$ colloidal templates, assembled in chiral nematic domain using optical tweezers. Defect lines are clearly visible between crossed polarizers, therefore one can easily reconstruct their spatial ordering. The schematic drawings of defect entanglements were made by KnotPlot software [266]. Relaxation mapping from the initial physical conformation to the final minimal planar projection was performed under topology-preserving Reidemeister moves, implemented in a simple dynamic algorithm. Knots and links are classified according to the traditional Rolfsen notation [174]. Scale bars correspond to $5 \mu\text{m}$.

The true variety of interlaced defect patterns has been realized when assembling larger particle arrays. Figure 5.18 shows a series of generically similar $p \times 3$ colloidal templates, supporting defect configurations in the form of various knots and links. More precisely, the entangled defect configurations share many common features and can be grouped into the same family of prime alternating torus knots and links [151]. Members of the torus family can be drawn without intersection on the surface of torus and they represent the most studied group of knots [150].

The physical defect conformation winding around colloidal particles is first redrawn as a planar projection in order to define its topological properties. When defect loop is flattened, defect segments produce only one type of crossing due to the specific geometry of the twisted nematic cell. Therefore, the defect line close to the substrate is always aligned perpendicularly to the rubbing direction. Consequently, the crossing on a single colloidal particle is always of the same type; negative or left-handed in the left-twisted nematic domain. These crossings are further used to identify and to characterize different forms of entanglement. To facilitate the analysis, the physical conformation of interlaced defect loops has to be represented with the minimum number of crossings [151]. The transformation from the initial physical conformation to the final minimal planar projection of the particular knot or link is schematically illustrated on the right side of Fig. 5.18 for five different colloidal arrangements. One can observe that coils at the edges of the entangled conformations form incidental crossovers, which are simply eliminated by the application of Reidemeister moves. Additional disentangling is performed through the sequence of topology-preserving twists and bends, implemented in a simple dynamic algorithm within a package for representing knots [266]. Finally, one obtains the minimal planar projections of knots and links, characterized by the crossing number, which is in this case equal to the number of rows p . We started with two laterally linked figure of eight chains, consisted of three colloidal particles, forming the Hopf link [see Fig. 5.18(a)], and continued by attaching the third figure of eight chain. The assembled structure resulted in the left-handed trefoil knot with three distinct crossings, located in the middle column of 3×3 colloidal arrangement, as clearly evidenced in Fig. 5.18(b). The crossings on colloids without handles thus crucially influence the topology of entangled defect loop, whereas the particles with handles only support strained defect conformations. Insertion of another row of three laterally entangled colloids has further increased the number of crossings, which has resulted in the famous Solomon link [see Fig. 5.18(c)]. Following the same way of knitting, one can ascertain that combination of even p and odd q provides two-component torus links, whereas odd p and odd q combinations give rise to alternating prime torus knots. The term 'alternating' signifies a geometric characteristic of the alternating nature of subsequent crossings in the minimal planar projection. These are the simplest linked forms because all the crossings are equivalent in sign and placement.

Helical defect coiling in our assemblies has, in addition to sign, a handedness ascribed by the familiar 'hand rule' of physics. Since all the crossings in the physical conformations of knots presented in Fig. 5.18 are negative, the coiling defect segments in the form of single and double helices are left-handed. It is interesting to note that even though all constructed torus knots have a negative writhe number, all two-component torus links in minimal planar projection have positive writhe and therefore possess the opposite handedness within the same nematic domain. Surprisingly, in all cases the segments of defect loops have a form of single and double helices, otherwise widely adopted by nature as essential structural elements of biomolecules such as DNA and proteins. Recently, it has been shown by Maritan *et al.* [267,268] that such conformations correspond to the optimal shapes of closely packed elastic strings in strongly confined space. The emergence of such motifs in our experimental system is in fair agreement with their numerical simulations, while the interplay between the entropy and the elastic energy inside confined chiral environment strongly prefers the helical ordering of entangled defect lines. Since passing lines induce the same type of elastic distortion, they locally repel each other and thus additionally strengthen the entangled colloidal structure. The non-zero thickness of entangled lines is important as well because it has two possible effects. Firstly, the defect segments cannot be bent too sharply and secondly, any two points that are far apart along the defect line cannot be too close to each other in space. These conditions are spontaneously fulfilled in our system because here presented interlaced patterns are assembled from discrete twisted loops, which are only slightly deformed during the incorporation into larger structural motifs. In contrast to uniform nematic field, the geometry of a twisted nematic cell facilitates the entanglement by shifting apart the top and bottom defect strands.

In addition, entangled defect loops in a nematic liquid crystal are not just simple strings, but they offer, beside the mainstream topology of entangled curves, also a tool for the largely unexplored studies of knots made from ribbons or elastic belts [222]. Such ribbons themselves carry two topological invariants, winding number and topological charge [120,121], which both stem from the molecular orientation profile around the loops and allow their effective topological visualization in terms of differential geometry. Whereas distortions in a form of Möbius strip and two interlinked defect rings have already been reported and topologically analyzed in cholesteric liquid crystal many years ago [269,270], there seems to be another opportunity for theoreticians to continue with the analysis of much more diversified topological conformations.

5.3.3 Topological analysis of entangled particle arrays

From planar tiles to reconfigurable trivial tangles

In the previous Section we have focused on prime alternating torus knots and links entangled around regular $p \times q$ arrays of colloidal particles. Here, we shall show that the structural variety of topological objects in the studied system is enormously rich and that it comprehends many other knot families with a huge number of topological isomers. Unfortunately, more complex entanglements consisting of numerous crossings are not easy to identify and one cannot classify them without applying mathematical rules.

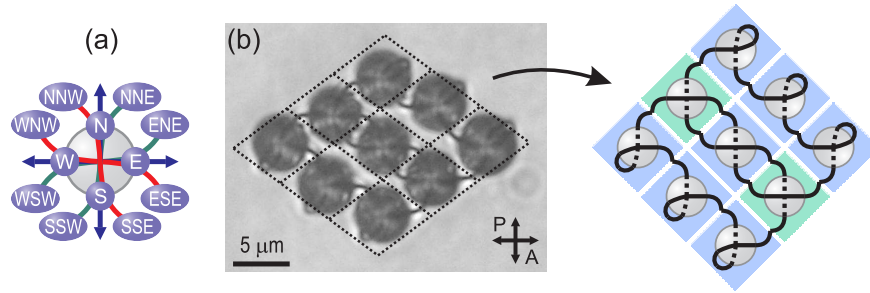


Figure 5.19: Construction of basic structural elements. (a) One can assign four compass directions $\{N, E, S, W\}$ to four intersections between defect strand and the edge of the particle. These four endpoints are further split in three directions due to elastic bending of defect strands. (b) Arbitrary 2D entangled colloidal structure can be then cut up to separate pieces with the corresponding orientational profiles of defect strands. Different particles are connected with a different number of neighboring particles.

We started our analysis with a Saturn ring that forms spontaneously around a single colloidal particle. Since the ring is twisted in a shape of the figure of eight, it always produces a crossing of defect strands in the middle of the particle. This crossing remains intact during the optical micromanipulation because we always grab and cut solely the handles of the Saturn ring. Thus, the orientational profile of the liquid crystal is significantly deformed only in the vicinity of the colloidal surface and the cut up defect strands adopt only appointed spatial directions, presented in Fig. 5.19(a). We have ascribed four compass directions to four intersections between the defect strand and the edge of the spherical particle. These four corner points can be further split in three directions due to elastic bending of the defect strands. Using the proper combination of orientational profiles around the individual colloidal particles, one can reconstruct the arbitrary 2D entangled colloidal structure; an example is shown in Fig. 5.19(b). Consequently, there exist up to 3^4 possible configurations with four free defect strands, positioned around a single colloid. We call them basic planar tiles since they represent fundamental structural elements of arbitrary 2D entangled colloidal structure in 90° twisted nematic cell. All possible tiles in left-twisted nematic domain are schematically illustrated in Fig. 5.20, starting with eight simple representatives in blue frames, which correspond to the corners. Next eight tiles, denoted by red frame, fit to NE or SW edge of the colloidal structure. These tiles have only two free defect

strands, therefore they can be connected with at most two neighboring tiles. The remaining 81 central tiles have four free defect strands and they can be connected either with two, three or four nearest neighbors. In addition, the green framed representatives are also the constituents of NW and SE edge of the structure.

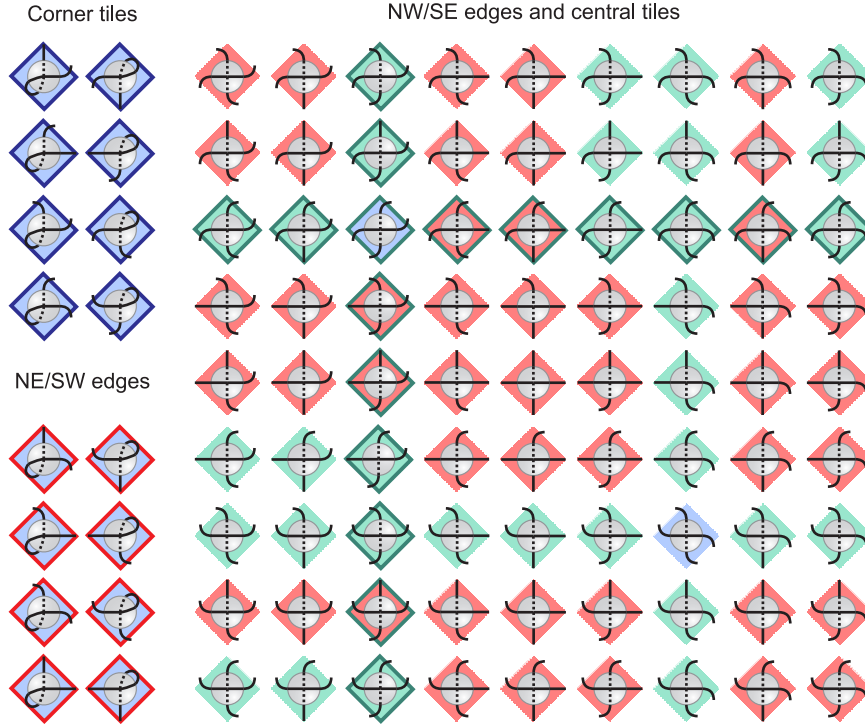


Figure 5.20: Basic structural elements of 2D entangled colloidal structures are schematically illustrated as planar tiles. Since there are four intersections between defect strands and the edge of the particle, which further split in three directions due to elastic bending, one obtains 3^4 different configurations with four free defect strands. Those on a blue background can be connected with two neighboring particles, those on a green background share defect strands with exactly three neighbors, whereas those on a red background bind with four different neighbors. Corner tiles are denoted by blue frames, whereas edge tiles are placed within green and red frames, respectively.

To assemble the arbitrary 2D entangled colloidal structure from the basic tiles, one has to follow several simple rules. It is obvious that a particular tile can not be connected with all available planar tiles because all defect strands have to catch each other in the right direction. Therefore, it is necessarily to find out those defect strands on the neighboring particles that properly stick together. Examples of regular tiling pattern are presented in Fig. 5.21. In the first example, four neighboring particles are connected with four straight defect strands, forming a crossing in the middle of the structure. Further examples demonstrate other options, where the middle of the structure is connected through two parallel defect strands, oriented in two perpendicular directions. It is important to note that when a single strand connection between two neighboring particles is assigned, also another one is simultaneously determined. Following the suggested rules, we have designed the computer program that searches for all possible combinations of basic planar tiles, organized on a $p \times q$ particle array. Surprisingly, we have found that all simulated entangled defect patterns up to 5×5 size of the template consist only from combinations of three particular tangles, which are schematically illustrated in Fig. 5.21 and defined in the following paragraph. This finding has substantially facilitated our analysis because it enabled us to use much smaller set of basic structural elements.

Thus, instead of planar tiles we have employed the concept of 2-string Conway tangles [177], which will denote any configuration of two unoriented arcs embedded within a given sphere. Then, we can easily identify three trivial tangles, denoted by -1 , 0 and ∞ , as shown in Fig. 5.22.

The fourth trivial tangle $+1$, which corresponds to the positive crossing, is omitted since it cannot be realized in the left-twisted nematic domain. Figure 5.22 shows three interlaced conformations, situated among 3×4 colloidal particles and differing only in the white encircled region. All defect conformations are assembled by addition of trivial tangles, which can be reconfigured using optical tweezers one into another by local 'surgical operations'. Effectively, this is achieved by breaking two defect segments, which happens as a consequence of the localized heating of liquid crystal with the laser light, and reattaching them in a different way during the controlled temperature quench [83], as schematically illustrated in Fig. 5.22. Such local reknitting is equivalent to the planar rearrangement of trivial tangles, which can cause the switch of chirality, affect the topological type or even change the number of loops in entangled object.

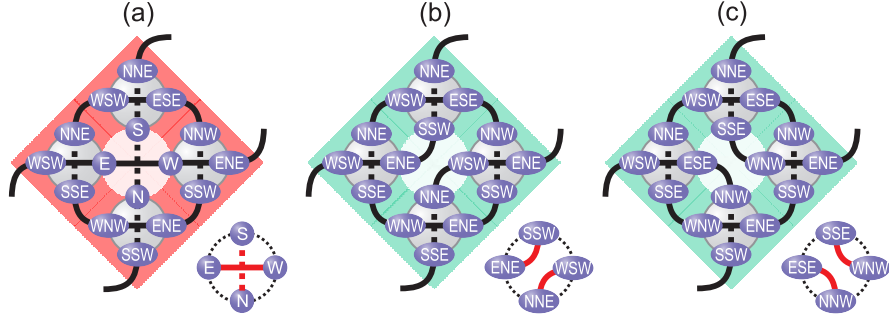


Figure 5.21: Instructions for assembly of basic structural elements. (a) Four basic tiles, connected through interparticle crossing. Each tile provides a single strand, which couples to the oppositely positioned defect strand, e.g. E-W. (b, c) Two other types of binding demonstrate connections through two parallel defect strands, oriented along and perpendicularly with respect to the edge of the structure. Orientations of particular strands are denoted by cardinal directions on the 16-point compass rose.

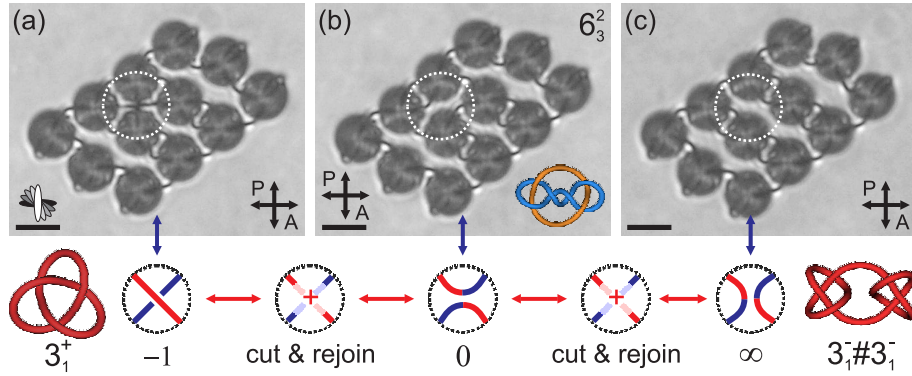


Figure 5.22: Conway tangles are basic structural elements of reconfigurable knots and links. Three distinct conformations of interlaced defect loops differ only in the white encircled region. These regions define three trivial tangles, denoted by -1 , 0 and ∞ , which can be reconfigured one into another by laser induced reorientation of nematic liquid crystal. The rearrangement of trivial tangles, schematically illustrated in the lower part of the image, yields structural and topological changes: (a) right-handed trefoil knot 3_1^+ is transformed to (b) two-component link 6_3^2 when -1 tangle is switched to 0 tangle. (c) Another transformation of 0 tangle to ∞ tangle yields the connected sum of two left-handed trefoils $3_1^- \# 3_1^-$. Scale bars correspond to $5 \mu\text{m}$.

Further on, we have focused on topological analysis of regular $p \times q$ colloidal templates, serving as a basis for all knotwork design. Demanding that each colloidal particle is connected either to two, three or four neighboring particles guarantees that completed knotwork is always properly woven in all allowed directions. Since defect lines can be folded in four principal ways, all possible permutations of trivial tangles must be employed in order to cover all structural motifs. In accordance with above defined rules, we were then able to empirically derive the number of

all well-defined entangled configurations on $p \times q$ colloidal template, described by equation:

$$N_{\text{configurations}} = 4^{(p-1)} 3^{(p-1)(q-3)}, \quad p \geq 2, q \geq 3. \quad (5.1)$$

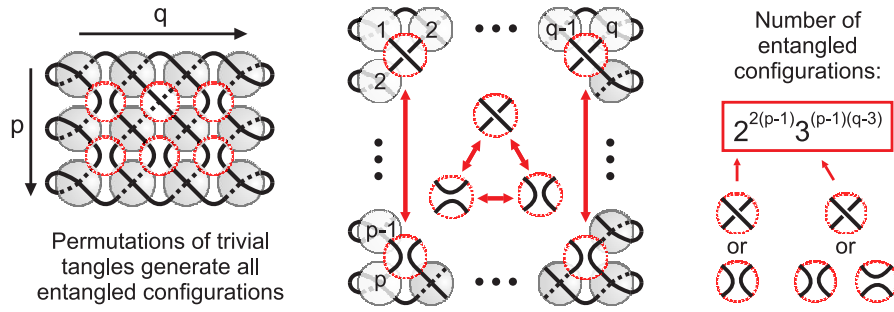


Figure 5.23: Construction scheme for all possible entangled configurations. One can cover all structural motifs on a $p \times q$ colloidal template by using all possible permutations of trivial tangles. The empirical derivation of Eq. (5.1) is directly evident from the presented illustration.

Applying the rules described above, one can easily calculate that 3×3 template supports only 16 distinct configurations, whereas 4×4 template generates already 1728 configurations and 10×10 template produces over $3 \cdot 10^{35}$ topological objects. Since the number of topological configurations increases so rapidly, we have focused our investigation to relatively small fraction of colloidal templates, having $p, q \in \{2, 3, 4\}$.

Knot classification and distribution of topological configurations

In order to distinguish and classify all possible knot types that could appear in a particular template, we have applied the concept of polynomial invariants from the knot theory [151]. Each randomly entangled pattern in a non-simple physical conformation was firstly redrawn in a program for representing knots [266]. Then, a simple dynamic algorithm, implemented in the same program, was used to obtain a minimal crossing projection, as illustrated in Fig. 5.24. Further analysis was carried out using the Kauffman states model [151,156]. The method involves enumeration of all possible states S_i in a knot diagram K , followed by the smoothing of each crossing by cutting it out and reconnecting it in a one of two possible ways: $A = \asymp$ or $A^{-1} = \frown$, resulting in $|S_i|$ closed circles. An example of Kauffman states for right-handed trefoil knot is presented in Fig. 5.23. All crossings were identified, each being an over-crossing and having $\varepsilon_j = +1$. These information are sufficient to calculate the Kauffman polynomial in the variable A by hand [156] or using the before mentioned computer program [266]:

$$X(K) = (-A)^{-3w(K)} \sum_i \langle S_i | K \rangle (-A^2 - A^{-2})^{|S_i|-1}. \quad (5.2)$$

Here, the sum covers all possible states of S_i , while $\langle S_i | K \rangle$ denotes the product of all A and A^{-1} at the crossings, and $w(K)$ corresponds to the total writhe number [151]. Thus, the Kauffman polynomial of the right-handed trefoil is equal to $X(K) = A^{-7} - A^{-3} - A^5$. Finally, the Jones polynomial was obtained simply by using the substitution $A \rightarrow t^{-\frac{1}{4}}$ [175]. For other entanglements the obtained expressions were compared to the polynomials in the enumerated Table of Knot invariants [271] in order to correctly define their topological type.

In a small collection of topological conformations we have identified the majority of prime alternating knots and links having minimum crossing numbers, ranging from 2 to 6. The first Hopf link appears on a 2×3 template, while the simplest trefoil knot is entangled around 3×3 colloidal particles. The distributions of topological configurations on the 4×3 and 3×4 colloidal templates are presented in Fig. 5.25.

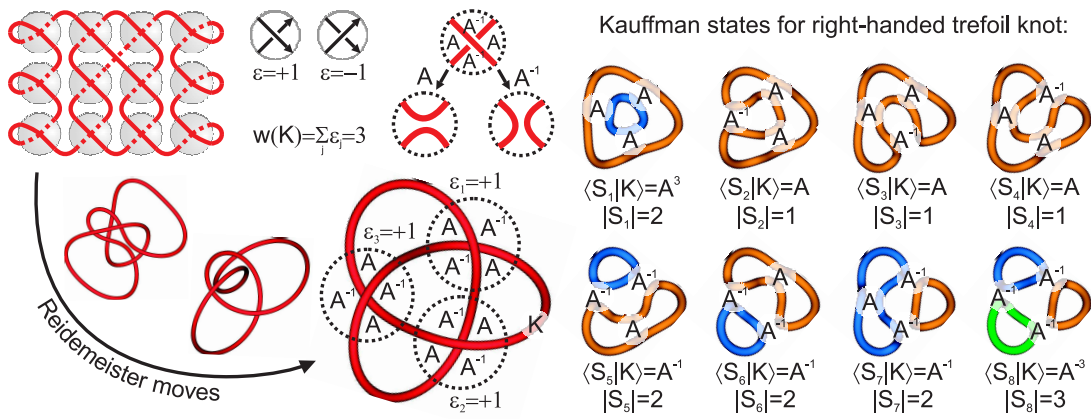


Figure 5.24: Construction of Kauffman states for right-handed trefoil. Firstly, the physical conformation is relaxed into minimal planar projection by Reidemeister moves and writhe number $w(K)$ is calculated. Then, each crossing is smoothed in one of two states, A or A^{-1} . Finally, all possible combinations of obtained states determine a state of the knot as a whole. $\langle S_i | K \rangle$ is the product of all A and A^{-1} at the crossings and $|S_i|$ corresponds to the number of circles in the resulting link diagram.

On the 4×3 template more than 50 % of all possible conformations is equivalent to the unknot and only 6 % corresponds to the trefoil. The portion of links slightly exceeds 20 %, however, it is also limited to two simplest representatives, the Hopf link and the Solomon link. As anticipated, the number of different knot types and the minimum crossing number increases substantially with the increasing length of defect loops. On a slightly larger 3×4 template we have identified 144 distinct entangled conformations. The fraction of unknots has dropped below 40 % and it has only slightly exceeded the number of links. One can observe four different link topologies with up to three interlinked components. Despite structural variety of links, the diversity of knots is still limited to trefoils and a single composite granny knot.

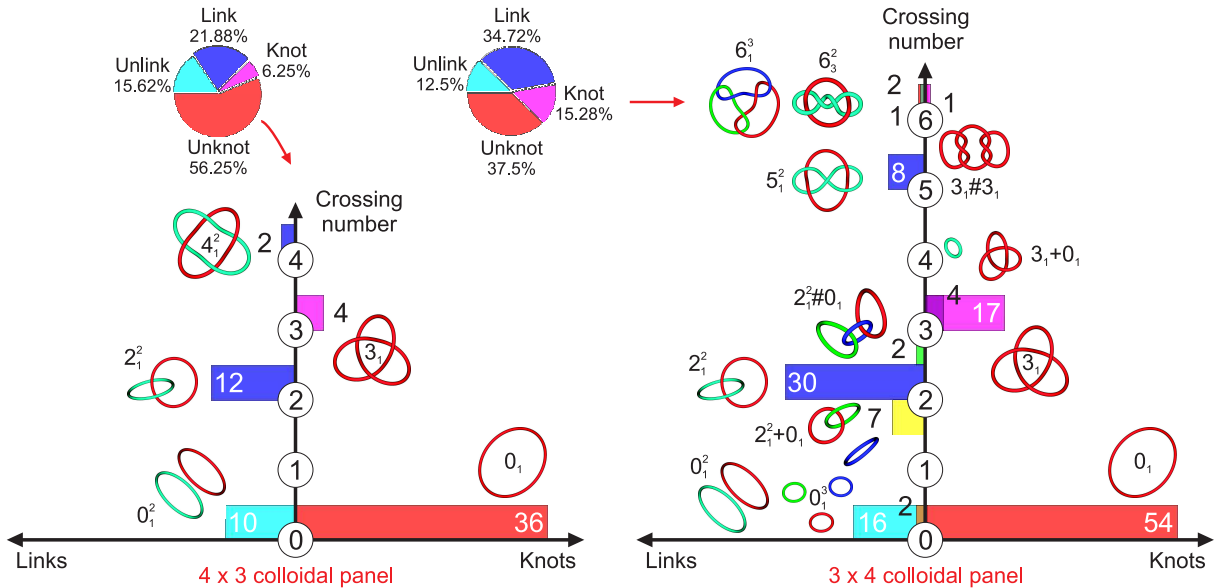


Figure 5.25: Distribution of topological configurations on the 4×3 and 3×4 colloidal templates. All knots and links are ranked according to the crossing number. The complexity and variety of knots and links is increasing with the length of the defect loops and consequently with the size of the template. Therefore, the fraction of linked and knotted objects increases as well, together with number of components. The strong prevalence of prime knots and links is rather surprising, because they are not the only possible type of knotting. However, they occupy 100 % on the 4×3 template and over 90 % on the 3×4 template.

The knotwork created on $p \times q$ colloidal templates is closely related to the basic weaving patterns. Moreover, our interlaced ornaments are very similar to the famous Celtic knotwork and differ from them only in the missing $+1$ trivial tangle [272]. Therefore, our fully interlaced patterns consist exclusively of -1 trivial tangles, which cover the entire template. Regarding the symmetry of such criss-cross knotwork, we have empirically identified several geometrical features, common to the arbitrary size of a $p \times q$ template. They are listed as follows:

- The number of entangled loops equals to the greatest common divisor of p and $q - 1$.
- If p and $q - 1$ have no common factor, then a single loop interlace the whole template.
- $p \times p$ square templates always support only one unknotted component.
- All entangled loops are topologically equivalent either to unknot or to unlink.

To obtain more elaborate designs, the regularity of this primal pattern has to be interrupted. As already discussed, this is achieved by smoothing the -1 crossings into two other trivial tangles, 0 and ∞ , respectively. When sufficient crossings are removed, the underlying plait ceases to be the dominant feature in the design and a pattern composed of knot motifs starts to appear. In this way, a bewildering assortment of interlaced designs can be created and for the time being, we were not able to determine the number of components for such arbitrary pattern. Intuitively, these patterns are collections of motifs arranged in a systematic fashion, but they are not discrete due to the continuity of the folding defect lines, so there is no obvious or natural way to split them up into the set of transitive symmetry groups. This inbuilt regularity and the imposition of periodicity means that many of the patterns have non-trivial symmetry. Despite the fact that mathematical analysis in terms of symmetry operations (rotation, translation, reflection) helps to identify topological isomers and consequently, substantially lowers the number of disposable topological objects, many open questions remain unanswered. For example:

- Is it possible to obtain non-alternating knots and links in our interlaced patterns?
- Do the regular arrangements of $p \times q$ templates prohibit the occurrence of achiral knots?
- Is it possible to predict the number of (un)linked components?

In short, it seems unlikely that resources of the entangled patterns would be exhausted in the near future, therefore there is still a room for imagination and creativity.

Reconfigurability of twisted nematic domains

Another intriguing feature of entangled colloidal structures in a twisted nematic cell includes the underlying bistable orientations of microscopic twist domains, that are topologically arrested among colloidal particles and defect lines. When observing the large entangled colloidal crystal between crossed polarizers with inserted optical compensator, the oppositely twisted domains appear as green and grey colored regions (see Fig. 5.26). The colors stem from left and right-handed twisting of the nematic director inside a particular domain. Furthermore, we assume that left and right-twisted domains must alternate to effectively compensate the topological charge imposed by the particles. This means that a left-twisted domain always appears next to the right-twisted domain, irrespective of the particle arrangement. The introduced elastic frustrations are namely the consequence of a distinctive spatial writhing of confined defect lines, governed by the perturbation of the director field [120,124]. The geometrical characterization of such defect conformations in an uniform nematic field has been discussed in analogy to triangular connected strips [222], however, more advanced visualization and topological analysis of 2D entanglements in a chiral nematic field is still under investigation.

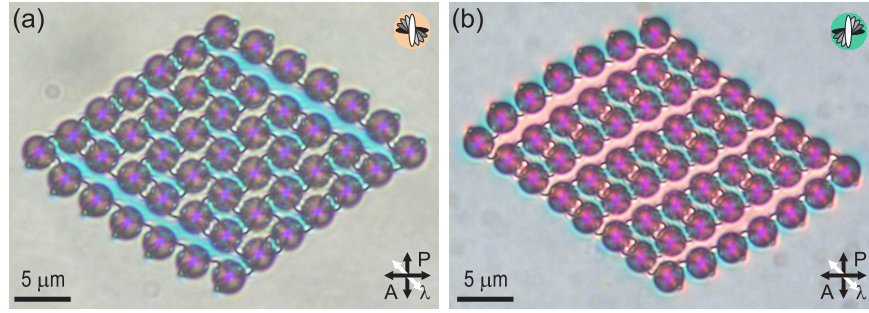


Figure 5.26: 2D entangled colloidal crystals present a diversity of alternating twisted nematic domains together with intriguing embedment of interlaced defect loops. (a) Symmetric arrangement of 7×7 particles supports an equal number of left and right-twisted domains, entangled by a single unknotted defect loop. (b) 7×8 colloidal particles are entangled with 19 interlinked defect rings. Different orientations of nematic molecules are clearly visible between crossed polarizers with inserted λ plate.

The useful aspect of twist domain colors is considered in a connection with a graph theory. It is well-known that there is a correlation between knot diagrams and edge-signed planar graphs with the potential to commerce in both directions [149,151]. To our surprise, 2D entangled colloidal structures in chiral nematic fluid provide a natural framework for the construction of shaded planar projections, as illustrated in Fig. 5.27(a). From the projection of entangled defect loops and colored domains among them, one can draw a planar graph as described. Since every other twist domain appears in the same color, one can put a vertex at the center of each green colored region and then connect with an edge any two vertices, positioned in regions which share a common crossing. Then, one can define crossings to be positive or negative based on the way they cross. Further on, one can label each edge with '+' or '-', depending on whether the edge passes through a positive or a negative crossing. The result is called a signed planar graph.

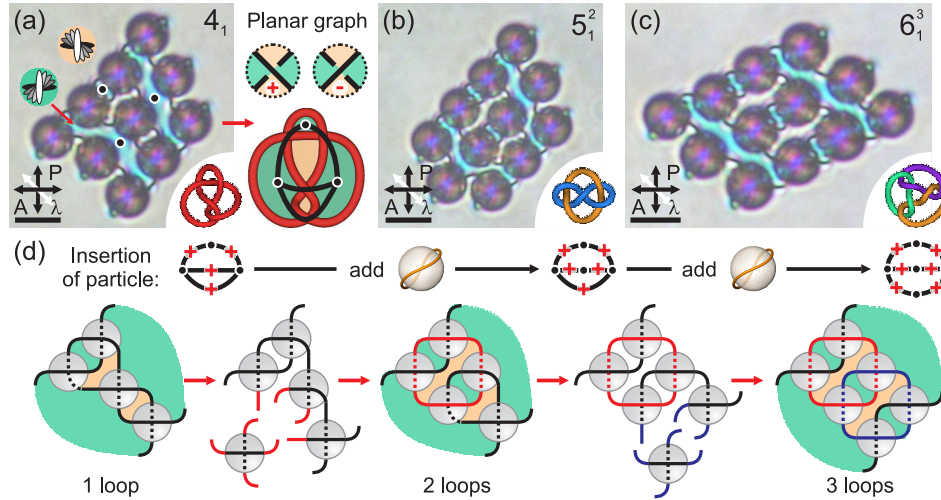


Figure 5.27: Oppositely twisted domains appear in two different colors, green and grey, when being observed between crossed polarizers with inserted λ plate. The colors spontaneously alternate according to direction of the local twist. (a-c) One can extract a signed planar graph from the optical micrograph by taking the green colored regions as vertices and the crossings between them as edges, labeled according to the sign convention. Since there is a correlation between knot diagrams and planar graphs, the entangled configurations can be recognized as knots or links. (d) When an additional particle is incorporated into the colloidal template, defect strands have to be reconfigured as illustrated schematically. Such reconfiguration influences the number of embedded domains and topological type of entangled loops, which is clearly evident also in planar graphs. Scale bars correspond to $5 \mu\text{m}$.

More detailed insight into constructed graphs reveals that insertion of an additional particle in

the assembled structure always brings one additional vertex and an extra positively-signed edge, as presented in Fig. 5.27(d). Moreover, by changing the number of particles, the topology of entangled objects can be reconfigured as well. For example, the figure-8 knot 4_1 is transformed into the Whitehead link 5_1^2 when a single particle is inserted in the middle of the structure. The defect strands have to be locally reconnected and consequently another loop with an additional twisted domain appears. Furthermore, the insertion of an inter-colloidal crossing, equivalent to the creation of a -1 trivial tangle, also results in an additional vertex and an extra negatively-signed edge in the corresponding graph. To illustrate this, we have constructed all possible shaded planar projections on 3×3 colloidal template, accompanied by the signed planar graphs, as schematically illustrated in Fig. 5.28. Interestingly, the position of inserted colloidal particle or created inter-colloidal crossing is directly reflected in the graph. Therefore, one can easily distinguish between all structural isomers, whose signed planar graphs have the same number of vertices and equally-signed edges. Using the planar symmetry operations, in particular rotation and reflection, it is straightforward to reveal the resemblance among entangled patterns. For instance, one can find a single trefoil knot and four topologically equivalent two-component unlinks among 16 entangled conformations in 3×3 colloidal template. All other entangled configurations correspond to the trivial unknot despite having a different number of vertices and edges. Some patterns are self-reflective and some can be reflected over the vertical axis one to another. The recognition of prime alternating knots and links is even additionally facilitated because all edges in their signed planar graphs always have the same sign [149,151].

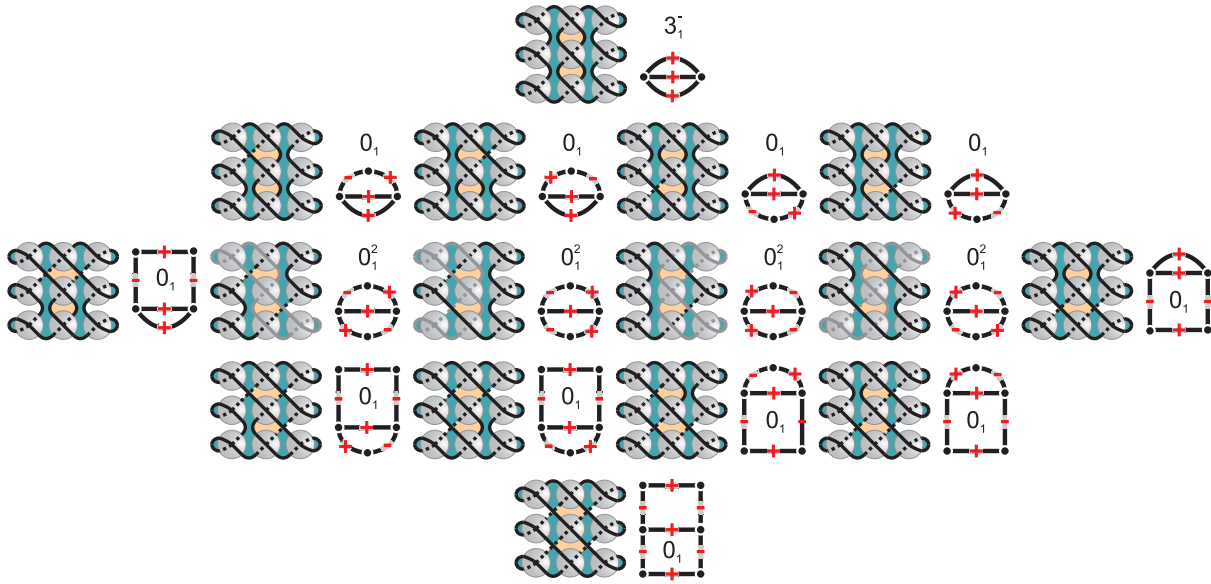


Figure 5.28: Shaded planar projections, accompanied by edge-signed planar graphs, on 3×3 colloidal template. Signed planar graph is extracted from the entangled projection by taking the green regions as vertices of the graph and joining them by edges over the common crossings. The edges are finally signed according to the sign convention, illustrated in Fig. 5.27(a). The insertion of a negative inter-colloidal crossing is directly reflected in the construction of the graph. It is interesting to examine all hidden symmetries of entangled patterns, which indicate the topological relatedness among them.

To conclude, we have briefly described a way from knot projections to signed planar graphs. Frequently, it is useful to turn questions about knots into questions about graphs, especially when investigating similar entangled patterns. One of the open questions in this respect is to find a practical algorithm for determining if a given projection corresponds to the unknot [151]. This is equivalent to asking whether there is a sequence of Reidemeister moves that takes us from the given projection to the unknot diagram. Eventually, we can turn Reidemeister moves into operations on graphs and hope that such approach will bring us closer to the final success.

5.3.4 Defect sequence coding and site-specific recombination

In the previous Section, we have been focused on topological analysis of various knot and link conformations entangled around $p \times q$ colloidal templates. We have found the way to identify arbitrary entanglement by means of mathematical theory of knots and calculated the number of all possible configurations, together with several interesting topological properties. We have shown that topology of entangled loops can be reconfigured by the incorporation of additional particles or by applying the rearrangement of trivial tangles. So far, we have dealt only with a graphical representation of entangled patterns, however, often it is also important to implement the information about topological order as a written code.

There is a great example in nature, where genetic information is stored as a sequence of base pairs, attached to the backbone of two long polymer strands, entwined in the shape of a double helix and known as a DNA molecule [162]. The main role of DNA molecules is the long-term storage of information. A DNA sequence, determined by the particular pairing and the sequential ordering of four nucleotide bases (A = adenine, C = cytosine, G = guanine and T = thymine), is often compared to a splicing code, because it carries the instructions required to build other components of cells, such as proteins and RNA molecules [163]. The DNA segments that carry this genetic information are called genes, while other DNA sequences have structural purposes, or are involved in regulating the use of this genetic information. Therefore, the base-pair sequence also significantly influences the topological conformation of DNA molecules [158]. Analogously to the DNA example, where there is an evident link between topological characteristics and a DNA coding sequence, we were stimulated to establish the connection between entangled defect segments and unique written record of their orientational ordering. To start with the basic structural element, we have selected a twisted defect ring, encircling a single colloidal particle, and have cut it at two sides, thus forming four free defect strands. Each strand was assigned a single letter, namely A, B, C and D, as shown in Fig. 5.29(a). Thus ascribed letters form the basis for orientational coding of defect segments.

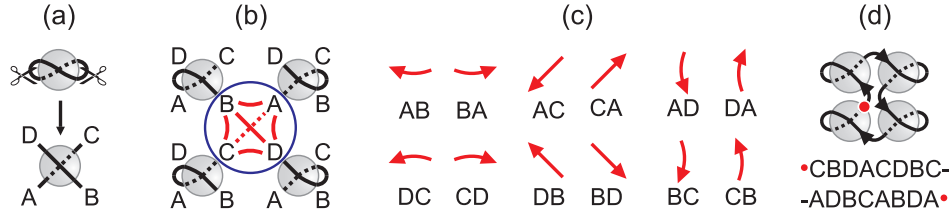


Figure 5.29: Orientational coding of defect segments by the sequence of letters. (a) Twisted defect ring is first cut at two sides, forming four free defect strands. Each strand is assigned a single letter, namely A, B, C and D. (b) There are six specific connections between the neighboring particles, denoted by red color, and organized in three trivial tangles inside a blue circle. (c) Assigning the orientation to the six connections, one obtains a dozen of oriented segments, represented by a distinctive set of letter pairs. (d) Defect sequencing starts from arbitrary chosen position, denoted as a red dot, and follows the shape of an entangled loop. The sequence of letters corresponds to the unique record of the topological form.

We have continued with specifying connections between the neighboring particles. There are six specific links, illustrated in Fig. 5.29(b), forming three trivial tangles, to which orientation can be assigned. Consequently, a dozen of oriented segments are formed, presented by distinctive set of letter pairs, as shown in Fig. 5.29(c). Such defined defect segments represent an effective tool that enables the unique description of arbitrary entangled configuration by constructing a word in the letters $\{A, B, C, D\}$. An example is presented in Fig. 5.29(d). From the randomly chosen starting point, denoted as a red dot, the form of entangled loop is followed and a sequence of letters is recorded, respectively.

Further on, the concept of sequencing has been applied to elucidation of the hidden structural relationships between adjacent topological defect conformations, entangled around $p \times q$ colloidal

template. As an example, we have selected a 3×3 template, entangled with a single defect loop and possessing a form of the unknot 0_1 . Initially, the defect loop was sequenced to obtain the word in letters and then a single reconfiguration of the selected trivial tangle, denoted as green colored region in Fig. 5.30(a), has been performed. Consequently, another topological object in a form of the trefoil knot 3_1 has been obtained and afterwards sequenced to the corresponding assembly of letters. By observing the changes in graphical representation it is possible to find out which type of structural transition has occurred, while applying the written code additionally explains that a concerned part of the letter sequence has been reversed, as schematically illustrated by the green colored text in Fig. 5.30(a). For the described structural transition the term *inversion* is used, since it reflects both the inversion in a sequence of letters, as well as the inversion of the orientation in a concerned defect segment. In addition, we have identified another type of structural transition that is always accompanied by the change of topological type as well. In this transition, termed as *exchange*, the orientation of involved defect loops remains intact, while the number of loops is either increased or decreased by one. Thus, this topological change switches between (un)knots and (un)links. The term exchange corresponds to the exchange of two sections in a letter sequence, denoted as red and blue colored text in Fig. 5.30(b), while it is scarcely observed in a graphical representation, where only the adjacent defect strands are juxtaposed.

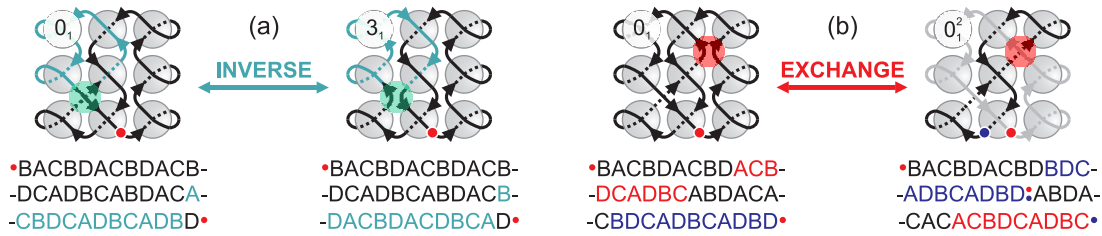


Figure 5.30: Site-specific recombination of defect strands using optical tweezers. (a) The entangled defect loop, possessing a topological form of the unknot 0_1 is initially sequenced to obtain the corresponding assembly of letters. Then, a site-specific recombination of particular strands is performed, yielding a new topological object in the form of the trefoil knot 3_1 . One can observe that the formed structural transition reverses the orientation of a particular defect segment, which is clearly reflected in the inversion of the green colored sequence of letters as well. Therefore, this type of transition is termed as 'inverse'. (b) Another topological transition takes place when two adjacent defect strands are exchanged. This transition preserves the orientation, however, it changes the number of components by one. It is termed as 'exchange' because it corresponds to the exchange of two (red/blue) parts in a letter sequence.

Similar structural transitions are commonly performed on a molecular level due to manipulation of a DNA molecule in the cell nucleus. Since the packing of DNA into the nucleus is very complex, topological constraints may often cause many problems, which reflects in different forms of topological entanglement, including limitless number of distinguishable knots and links. This entanglement interferes with, and is exerted by, the vital processes of replication, transcription and genetic recombination [162]. The biological solution to the entanglement puzzle is the so-called *site-specific recombination*, which is one of the possible ways for nature to alter the genetic code [158]. It is performed by enzymes called recombinases, which promote recombination function in topologically interesting and non-trivial ways. They either break a pair of DNA strands and recombine the ends by exchanging them or they integrate a block of alien DNA into a host genome [158,273]. As the name suggests, a site-specific recombination is the local operation, which involves tangle surgery. A pair of sites bounded by the enzyme always looks like a trivial tangle and can be replaced by another tangle. Even mathematical models exist that use tangles as building blocks for knots and links for computing the topology of circular DNA substrates involved in the individual recombination events [273]. These models work well in the case of several most studied recombinases, such as Tn3 resolvase and bacteriophage λ integrase, however, they can not be simply generalized to other enzyme families [158].

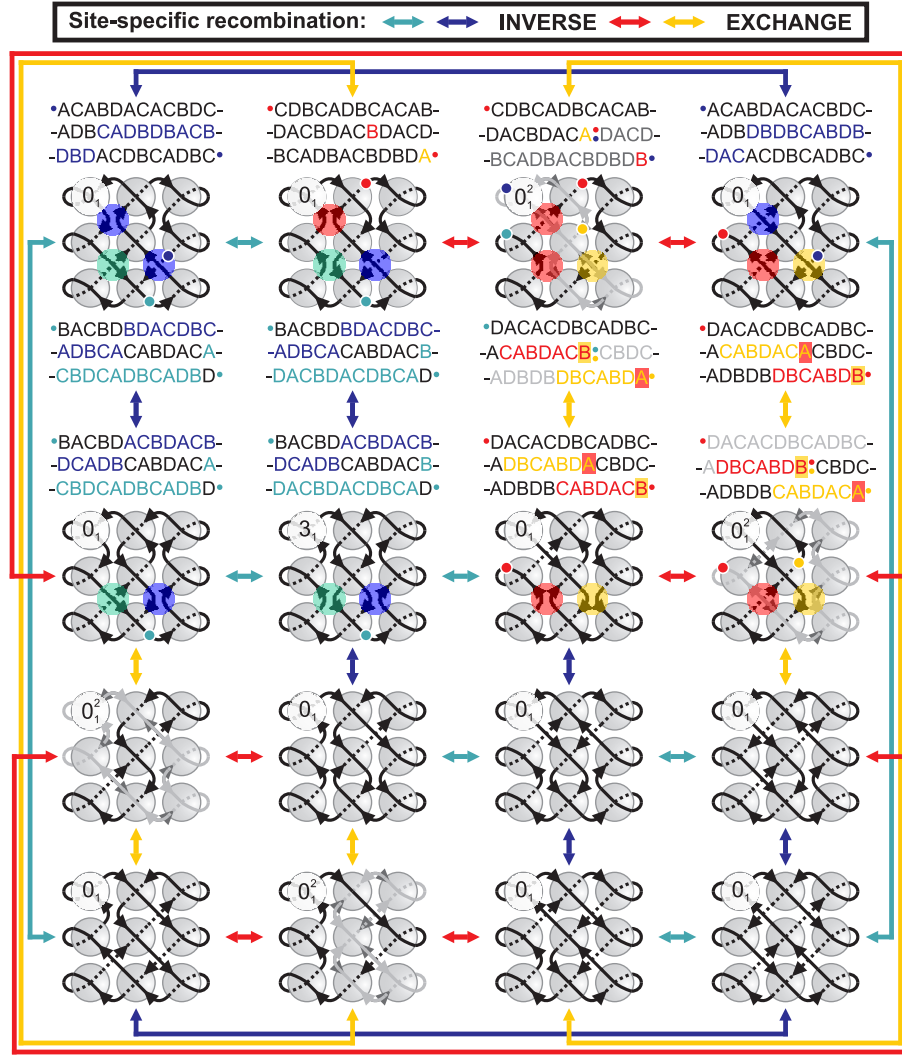


Figure 5.31: Overview of structural transitions among adjacent defect patterns on a 3×3 colloidal template, governed by a site-specific recombination of trivial tangles. To each individual loop the orientation is assigned and the corresponding sequence of letters is adopted accordingly. Due to the loop closure and the sequence periodicity, the starting point of a sequence, denoted as a colored dot, might be arbitrary selected. Then, a single recombination event is performed through the replacement of a trivial tangle. Depending on the underlying structure and the site of the recombination event, either inverse (green/blue double arrows) or exchange (red/yellow double arrows) occurs. Interestingly, one can always find such a combination of adjacent letter sequences that can be controllably transformed one to another using one of the two mentioned structural transitions. Unfortunately, topological transitions among adjacent patterns can not be completely explained only by structural changes. Rolfsen knot type notation is adopted [174].

In comparison to the biological examples, the advantage of our experimental system lies in the fact that we are not limited by the specific action of particular enzymes, but we are able to perform a site-specific recombination using optical tweezers on a known set of topological conformations. While DNA knots can be distinguished from unknotted forms only indirectly by agarose gel electrophoresis and subsequent electron microscopy [153,158], we are capable to recombine defect strands in a real time and directly observe the structural changes under polarizing optical microscope. Moreover, the structural transitions on $p \times q$ templates are not fully determined by the change of a tangle type, but they are rather characterized by the specific site of the recombination event. For example, in Fig. 5.31 the complete set of entangled configurations on the 3×3 colloidal template, together with all possible structural transitions among adjacent defect patterns, is presented. According to Eq. (5.1), there are 16 distinct topological

conformations, distributed over 11 unknots 0_1 , 4 unlinks 0_1^2 and a single trefoil knot 3_1 . If we start with the trefoil, which is characterized by four ∞ tangles, and recombine an individual tangle into a -1 crossing, the unknot is always obtained. But if we further perform the same recombination event on one of the produced unknots, we will obtain either unknot or unlink. Thus, in the case of an unknot the occurrence of crossing does not affect the integrity of the entangled loop, whereas the same type of a structural change at a different site might yield decomposition of a single loop into two separate components.

We have also noticed that the number of structural transitions among adjacent topological configurations strongly depends on the number of tangles that can be recombined at a particular site. For instance, on a 3×3 colloidal template, there are only four sites, where -1 and ∞ tangles can be recombined between each other. Generally, the number of structural transitions on a $p \times q$ template can be determined by the following equation:

$$N_{\text{transitions}} = N_{\text{configurations}}(p-1)(1+(q-3)), \quad p \geq 2, q \geq 3, \quad (5.3)$$

where the $N_{\text{configurations}}$ was already calculated by Eq. (5.1). One can estimate that there are 32 structural transitions among 16 topological configurations on a 3×3 colloidal template, presented by colored double arrows in Fig. 5.31. Different colors denote the type of structural transition and can be interpreted either as inverse (blue/green arrows) or exchange (red/yellow arrows). Surprisingly, in our experimental system the application of these two recombination rules can entirely explain any structural transition between two adjacent entangled defect configurations. Thus, by following the instructions described in a caption of Fig. 5.30, one can easily examine the relationships between different topological objects. Regarding the example in Fig. 5.31, one can ascertain that only two topological transitions are possible, namely $0_1 \rightleftharpoons 3_1$ and $0_1 \rightleftharpoons 0_1^2$, while the $0_1 \rightleftharpoons 0_1$ transition does not change the topology of entangled loop.

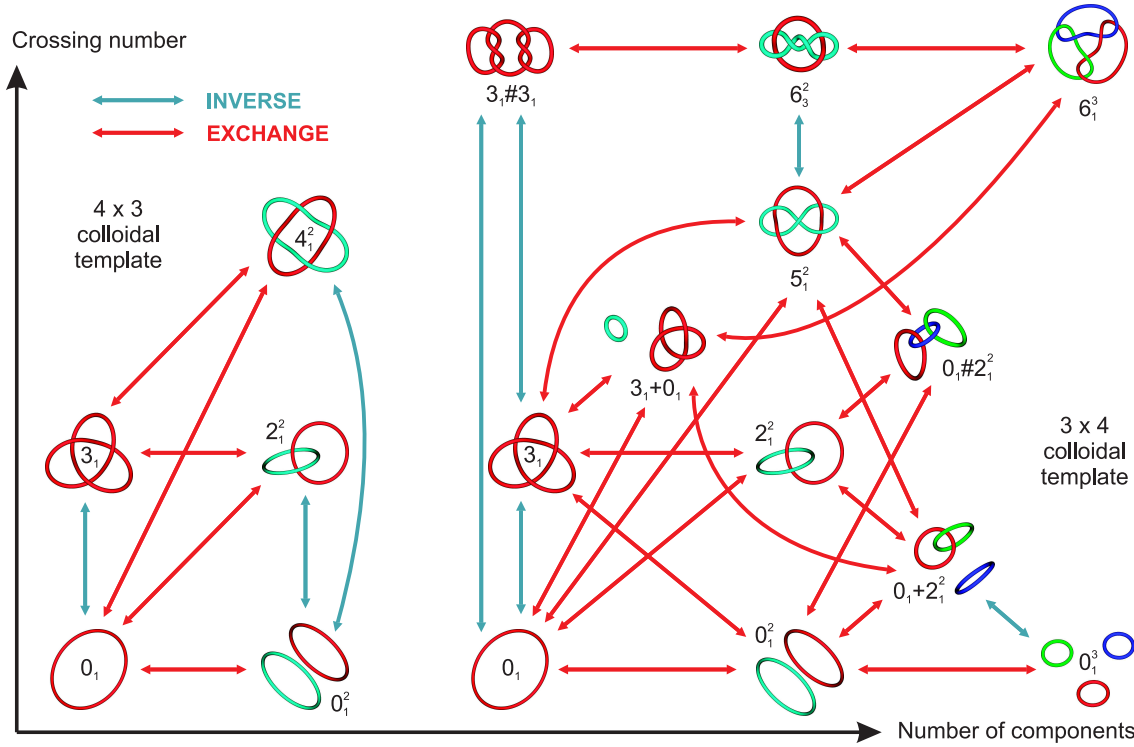


Figure 5.32: Topological transitions among topological configurations on the 4×3 and 3×4 colloidal templates. The configurations are organized according to the crossing number and the number of loops. The prevailing part of exchange is not surprising because a large portion of structural transitions which do not change the topological type is omitted from the presentation. All configurations are closely related, because there are only two recombination events required to completely unknot any of them.

On the basis of the described example, we are proposing a natural classification of knots based on their intrinsic position in the knot space. The latter is defined by the set of knots, to which a given knot can be converted by a single recombination event. Two instructive examples of such classification on the 4×3 and 3×4 colloidal templates are presented in Fig. 5.32. There are five different topological configurations, entangled around a 4×3 template, which can be reversibly reconfigured one to another. While any non-trivial configuration can be directly transformed to the unknot, there is no direct structural transition between the unlink and trefoil knot or between the Hopf link 2_1^2 and the Whitehead link 4_1^2 . It is also evident that inversion occurs when the number of loops is preserved, whereas exchange switches between (un)knots and (un)links. Another example on a 3×4 template shows a greater diversity of structural transitions and it is obvious that exchange highly exceeds the inverse. This finding is not surprising if we recall that in this case there is only 15 % portion of knots and that a large share of altogether 576 structural transitions which do not change the topological type of entangled patterns is omitted from the presentation. Therefore, the found relationships between the presented knots and links are mainly the consequence of a particular rearrangement of trivial tangles, as well as the size and the shape of a colloidal template. Interestingly, there are only two recombination events required to completely unknot the arbitrary entangled configuration. In any case, this is in agreement with almost 40 % cases of unknots, entangled around particular colloidal lattice.

However, we assume that more thorough investigation of structural transitions would bring us closer to the specific rules, which would determine the permitted topological transitions. Because the defect segments are entrapped between confining surfaces and thus cannot pass through each other, the principles of topology dictate that knots can only nucleate through the adequate weaving of adjacent segments. This observation corresponds closely to the mathematical representation of knots in a braid diagram, while the weaving could be connected to braid moves, both providing some additional insights [151]. A braid diagram and a knot are related by established the connection among the group of line segments, as indicated by the dashed lines in Fig. 5.33. One may ascribe a single line to the exterior edges due to their inability to change the topology of the pattern, while two interlaced lines may be ascribed to the interior space. Further on, one can assume that the end segments make random weaves, with a 50 % probability of moving left or right, forming only a single type of crossing. As demonstrated in Fig. 5.33, such model would allow for both knotting and unknotting to occur. The identification of the weaving braids can be performed through Dehornoy algorithm for comparing braids [151], which should effectively recognize at least the simplest unknots. Unfortunately, to date we have not tested the proposed model and therefore have not been able to establish the general rule that would completely elucidate transformations among arbitrary topological entanglements.

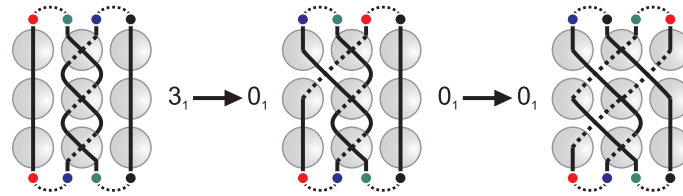


Figure 5.33: Schematic illustration of the simplified model for structural transitions and knot formation. Because of regular colloidal arrangement, the defect lines tend to align parallel along a certain direction and cross only in one way within the confined colloidal lattice. As discussed in the text, we can model knots during formation due to random series of braid moves of the end segment among the adjacent segments (look at different positions of colored dots). Various weaving patterns correspond to different topological types, presented by traditional Rolfsen notation [174]. The overall connectivity of the segments is indicated by the dashed line.

From the applied point of view, it is worth to mention that defect loops in chiral nematic colloids are non-material objects having an inherent property to attract material objects, such as small

particles or macromolecules. Such behavior is universal and has been demonstrated for trapping of colloidal particles in hierarchically organized superstructures [82] and for stabilization of the liquid crystalline blue phases by nanoparticles doping [92,95]. Defect loops in a liquid crystal produce 3D attractive potential, which exactly follows the topological form of the loop and can be as strong as 10 pN per micrometer-sized inclusions [82]. Effectively, entangled loops therefore act as confining tubes for (sub)micrometer inclusions, with their diameter given by material parameters and a temperature, typically in the range of 100 nm. Consequently, entangled defect patterns in chiral nematic colloids could be used as 3D manipulators for confining and knitting microscopic objects in topological subspaces of knots and links. For example, by confining the polymer filaments or DNA strands into the linked and knotted defect regions, their reptation motion could be effectively studied for various conformations [154,274,275]. The diameter of the reptation tube of the polymer or DNA strands would be simply controlled by the temperature and local manipulation of optical traps.

In conclusion, the facile creation of knots and links of various families makes chiral nematic colloids a strong platform for studies of knot and link topologies. Moreover, it represents the real manifestation of an abstract mathematical knot theory in concrete physical phenomena. Using regular particle arrays, we have optically observed and precisely controlled trivial tangles, as well as shaded link projections, which are both fundamental elements of the knot theory. By optical reconfiguration of various knots and links we have established the full control over available topological space and found two selective rules, which fully interpret the arbitrary structural transition. Finally, knots and links in chiral nematic colloids could find applications as (nano)manipulators in polymers, DNA and other biological systems in order to produce non-trivial spatial topologies.

Conclusions

The thesis deals with experimental studies of colloidal interactions and assembly of novel colloidal structures in confined nematic fluids. Experimental work was carried out using techniques of polarizing optical microscopy and optical tweezers, a micromanipulation tool, that enabled the complex colloidal ordering in two dimensions and crucially contributed to the explanation of these phenomena. To a large extent, the presented work was performed alongside with predictions and results of numerical modeling, accomplished by theoretical group at Physics Department, which assures a firm theoretical framework to the experimental achievements.

The aim of the thesis has been to explore colloidal interactions and to discover novel self-assembly processes in anisotropic fluids that could potentially lead to ordered periodic structures. The future technologies and devices require composite materials with well-controlled periodic structures and tunable electro-optical properties in micrometer and nanometer ranges, therefore we have focused our investigation to directed two-dimensional assembly of colloidal particles in thin nematic layers using optical micromanipulation. In particular, the research was aimed at: the measurements of interparticle forces, the (meta)stability of colloidal structures in uniform and non-uniform nematic fields, the assembly of periodic colloidal crystals, the analysis of liquid crystal ordering in the vicinity of non-spherical inclusions, the influence of induced disorder on defects binding entangled colloidal structures, the transitions among singular and non-singular topological defects and finally, the creation and explanation of complex topological entanglement in a form of linked and knotted defect lines.

The introductory part of the thesis, in particular Chapter 4, presents the results that have been obtained in our research group during the first two years of my postgraduate study. Though this research work has been initiated and accomplished by other coworkers, I have learned many important experimental skills and conceptual strategies, which have significantly influenced the evolution of my original ideas and subsequently enabled my independent research. My contribution was expressed through a detailed analysis of collected experimental data, in particular through the calculation of quadrupolar interparticle potentials. These results have shown that colloids inducing quadrupolar order, assemble into weakly bound hexagonal colloidal lattice, whereas colloids inducing dipolar order organize into strongly bound anti-ferroelectric-like two-dimensional crystallites of dipolar colloidal chains. This was the first experimental realization of two-dimensional colloidal crystals stabilized by the binding mechanism of liquid crystalline elasticity. Then, we have tried to automate the assembly process by the application of external electric field, which enabled the massive and directed transport of colloidal particles on macroscopic scale. This technique has enabled the formation of dense two-dimensional colloidal crystallites, however, it turned out that such approach is scarce and limited for achieving regular and tunable 2D colloidal architectures. Furthermore, at a certain cell thickness, slightly larger than the diameter of the particles, we have confirmed the metastability and coexistence of dipolar and quadrupolar configurations. I have analyzed the influence of the confinement on the stability of particular colloidal configurations in a wedge-type planar cells and adjusted the

width of the coexistence region by varying the surface anchoring strength. The continuation of this work has opened the possibility to study the dipolar-quadrupolar interactions, which have led to the assembly of binary colloidal crystals.

Novel type of colloidal ordering was achieved by unique binding mechanism, where colloidal particles are entangled by delocalized hyperbolic defect lines after the fast temperature quench of the surrounding nematic fluid. This procedure was theoretically proposed within the Landau-de Gennes model and then experimentally accomplished by optical tweezers due to their ability to produce very localized and controlled heating. Three distinct configurations, namely figure of eight, figure of omega and entangled point defect, were experimentally confirmed for the particle pairs and I have performed a detailed statistical analysis of numerous quenching experiments, which has shown the relative occurrence of particular entangled structure. Moreover, I have suggested the more precise optical control over the realization of the final configuration, which has enabled more complex entanglements in chiral nematic colloids.

The central part of the thesis, in particular Chapter 5, presents the main results, which are organized in three independent Sections. These achievements are based on my original contributions and have been thoroughly accomplished by myself under the supervision of my mentor. In Section 5.1 we have shown that the symmetry of elastic distortion does not crucially depend on the shape of inclusion, but it is characterized mostly by the combination of the boundary conditions on the confining surfaces. Non-spherical colloidal particles disturb the uniform alignment of the surrounding nematic fluid, resulting in both a distinct equilibrium orientation and highly directional pair interactions. Depending on the equilibrium orientation and the strength of confinement, we have observed the dipolar and the quadrupolar type of elastic distortion in the vicinity of rod-like objects. Dipolar microrods with homeotropic anchoring of the nematic at its surfaces tend to align with its long axis parallel to the far-field director, whereas quadrupolar microrods orient almost perpendicularly to the rubbing direction. Using precise optical micromanipulation, the strength and the separation dependence of interparticle forces have been determined. These are in the range of interactions between colloidal chains, assembled from spherical particles of comparable size. Since the microrod is topologically equivalent to the microsphere, we have found the same stable pair configurations in an uniform planar nematic cell. Our results are in agreement with recent numerical calculations and they represent the first experimental investigation of structural morphologies around anisotropic objects, immersed in confined nematic layers. The results from other experimental groups, which followed our investigation, have shown that elastic colloidal interactions in anisotropic fluids are sensitive to the particle shape. Moreover, the particle shape may be even exploited to tune the aggregation dynamics and consequently to control the particle interactions. Thus, one can envision the design of such interactions for the assembly of various colloidal architectures, ranging from anisotropic aggregates to new types of colloidal crystals.

Section 5.2 is focused on the energetic stabilization of escaped vortex-like defect rings in a non-uniform chiral director environment. In contrast to the uniform nematic field, where the predomination of singular defects is observed, the chiral liquid crystal ordering in the geometry of a 90° twisted nematic cell profoundly alters the nature of colloidal interactions and propagates the formation of non-singular topological defects. Self-assembly of linear dipolar chains is strongly suppressed, while antiparallel elastic dipoles become unstable at short distances and spontaneously transform into inseparable particle pairs bound with a string-like potential of escaped hyperbolic defect rings. These rings have a cross section identical to magnetic hyperbolic vortices, which generate skyrmion ground states in magnetic metals. Moreover, they are chiral objects, elucidated by the mechanism of director escape into the third dimension. While escaped defect rings of the opposite handedness are inherently indistinguishable and rarely observed in the uniform nematic field, the chiral nematic ordering removes the degeneracy by the large energy splitting between left and right-handed colloidal pairs. The opposite handedness of the liquid crystal twist and the escaped hyperbolic defect ring results in a huge reduction of

the binding energy when compared to the equal handedness of both. In addition, the energy difference provides an elegant way to achieve the chiral selectivity in a given twist domain, which spontaneously promotes only the opposite direction of director escape. However, the pair interaction only weakly depends on the handedness of the rings and readily leads to the controlled assembly of novel two-dimensional colloidal crystals of pure or mixed chirality. These colloidal crystals have been assembled using optical tweezers and are thermodynamically stabilized by the intercalation of non-singular defect loops. We anticipate that in addition to the interesting optical properties they might exhibit super elasticity, large strain under constant tensile stress when being exposed to external electric field.

Moreover, we have experimentally demonstrated that the relative stability and metastability of entangled and non-entangled colloidal structures are reversed in a 90° twisted nematic cell. For a particle pair, we have found that the figure of eight configuration has substantially lower total free energy than the non-entangled configuration of two quadrupolar particles with encircled Saturn rings. It is even not necessary to perform a temperature quench in order to generate the entangled structure, but a suitable particle arrangement close to the equilibrium positions and external triggering of the liquid crystal flow are sufficient for spontaneous formation of entangled pairs and chains. Furthermore, twisted cell geometry also allows two-dimensional topological entanglement of colloidal particles, which opens the way to design a huge variety of complex colloidal structures.

The most exciting results of the thesis are extensively reported in Section 5.3, showing that knots and links of various complexity can be achieved and arbitrary reconfigured on a microscopic scale using optical micromanipulation of defect loops, entangled around colloidal arrangements in chiral nematic dispersion. To date performed knotting of flexible filaments in biological and soft matter systems has been extremely limited due to the inherent smallness of the objects and usually large but poorly controllable ensemble of topological configurations. In contrast to difficult experimental mastering of those systems, knots and links made from topological defects in anisotropic fluids are relatively easy to design and they can assume a variety of related structural motifs with interesting topological properties. We have performed a systematic study of diverse defect entanglements using the methods of mathematical theory of knots. Thus, we have discovered that by applying local transformations of basic structural elements one can reconfigure arbitrary topological conformations in a controlled manner and determine their inter-related recurrence. Many non-trivial conformations belong to the family of torus knots and links, however, several alternating achiral knots and multi-component links have been identified as well. Furthermore, by orienting the entangled defect lines, arrested among the confining surfaces, we have created the unique record of topological structure, encoded in the periodic sequence of letters. Then, by using tunable optical trapping we have been able to perform site-specific recombination of defect segments and, in principle, to identify every structural transition between adjacent topological conformations. Surprisingly, all structural transitions are based on two specific modifications of oriented defect strands, termed inversion and exchange, which are commonly performed on a molecular level by recombination enzymes that manipulate DNA molecules during the processes of replication and genetic recombination. More thorough investigation of structural transitions indicates that there must be specific rules which determine the permitted topological transitions. Unfortunately, to date we have not been able to establish the general rule that could elucidate transformations of arbitrary topological entanglement. However, we believe that our approach shall aid to elucidate the relationships between various knots and links and that it will substantially complement the knot theory applications. Nevertheless, the linked and knotted topological defects in chiral nematic colloids can find applications as a model system for the study of topological conformations in confined and chiral environment, as well as light-addressed optical switches, bistable nematic liquid crystal devices or as three-dimensional (sub)micrometer manipulators of dispersed biopolymers and nanoparticles.

In sum, nematic liquid crystal colloids are novel composite materials with fascinating and highly promising electro-optical and mechanical properties, involving a number of amazing structures, such as chains, two-dimensional clusters and periodic colloidal crystals. Structural forces exerted by the liquid crystal act as effective elastic forces that stabilize micrometer-sized particle arrangements with the binding potentials of the order of several $1000 k_B T$. The assembly mechanism is based on the minimization of changes in the nematic orientational order. Moreover, it is greatly adaptable to different materials and allows highly attractive self-assembly method for building regular colloidal structures. Furthermore, the assembly can be effectively controlled by application of external fields and there is no a priori limitation to expand the concept down to the nanoscale. The true potential of liquid crystal colloids depends decisively on the development of experimental techniques, which could enable the large-scale assembly of regular three-dimensional colloidal structures for new classes of tunable photonic devices.

The presented escaped and entangled two-dimensional colloidal structures in chiral nematic fields offer several exciting directions in particle assembly and provide a novel perspective on topological ordering in confined anisotropic fluids, which might be applicable also to three-dimensional structures. The further investigations should employ the variable confinement of liquid crystal flow, topographically patterned substrates and electro-optically induced interparticle potentials in order to control the complex collective dynamics of dispersed colloidal inclusions. Therefore, the future research will focus on the potential application of nematic colloids in optics, microfluidics and photonics, aiming at three-dimensional colloidal structures in highly twisted cholesteric materials with the goal to stabilize regular particle arrays, to understand their assembly process and to characterize their optical and mechanical properties.

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Publications related to the work described in the thesis

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- I. Muševič, M. Škarabot, U. Tkalec, M. Ravnik, and S. Žumer. Two-dimensional nematic colloidal crystals self-assembled by topological defects. *Science* **313**, 954 (2006).
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- U. Tkalec, M. Ravnik, S. Čopar, S. Žumer, and I. Muševič. Reconfigurable knots and links in chiral nematic colloids. To be submitted to *Nature*.

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- I. Mušević, M. Škarabot, M. Ravnik, U. Tkalec, A. Nych, U. Ognysta, V. Nazarenko, and S. Žumer. Optical manipulation of nematic colloids: wires, superstructures, and 2D crystals. *Proceedings of SPIE*, **7038**, 70381A (2008).
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Razširjeni povzetek

(Abstract in Slovenian language)

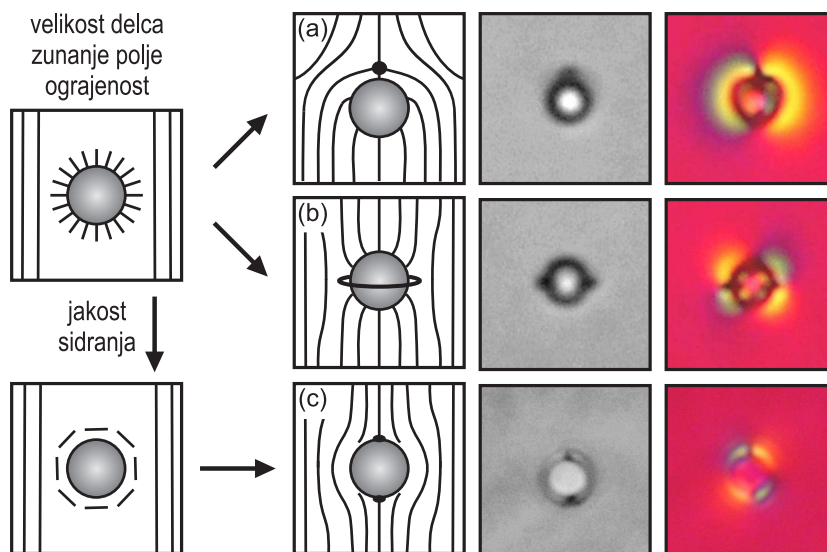
Uvod

Snov, ki jo običajno srečujemo v naravi, se nahaja v enem izmed razpoložljivih agregatnih stanj: plinastem, kapljevastem ali trdnem. Medtem ko v izotropni kapljevini ali plinu molekule zavzamejo celoten prostor in niso pozicijsko ali orientacijsko urejene, se v trdnem agregatnem stanju gradniki razporedijo v periodično urejene kristalne mreže. Vmesno stanje med izotropno tekočino in kristalno fazo imenujemo *tekočekristalno* stanje. Sestavljajo ga praviloma toge in nesimetrične organske molekule, ki se pri določeni temperaturi ali primerni koncentraciji molekul samodejno organizirajo na podlagi anizotropnih medmolekulskih interakcij in tvorijo nove *mezofaze* med tekočim in trdnim agregatnim stanjem. Mezofaze so določene z orientacijskim in možnim pozicijskim redom molekul. V dovolj velikem vzorcu se molekule v povprečju orientirajo v eno samo smer, ki jo imenujemo *direktor* $\mathbf{n}$, pri čemer sta v nepolarnih materialih orientaciji $\mathbf{n}$ in $-\mathbf{n}$ ekvivalentni. Najmanj urejena je *nematska* faza, kjer imajo molekule orientacijski red dolgega dosega, nimajo pa pozicijskega reda [1]. Če je tekoči kristal kiralen, direktor tvori vijačnico, fazo pa imenujemo *kiralna* nematska. Tekočekristalne faze, v katerih se molekule pozicijsko urejajo v plasti, imenujemo *smektične* [2]. Edinstvena lastnost tekočih kristalov je orientacijski red molekul dolgega dosega. Slednji se zvezno spreminja na velikostnem območju od nekaj nm do nekaj μm in je običajno močno odziven na vpliv zunanjih polj (temperatura, električno in magnetno polje). Ob prisotnosti površin, ki vsiljujejo nasprotujoče orientacijsko urejanje, se nematska faza deformira, kar velikokrat povzroči nastanek strukturnih napak ali *defektov*, v katerih se zvezno orientacijsko urejanje molekul zlomi. Defektna področja v nematskem tekočem kristalu predstavljajo linije ali točke [8]. Zanimanje za tekoče kristale se je močno povečalo po letu 1971 z zagonom proizvodnje tekočekristalnih zaslonov, ki danes predstavljajo več kot 90 % svetovnega trga optičnih prikazovalnikov. Njihovo uporabo v te namene je omogočila optična anizotropija in možnost spreminjanja orientacije tekočekristalnih molekul z zunanjim električnim poljem. Kmalu so se pojavili tudi prvi teoretični opisi tekočekristalnih faz, med katerimi sta najpomembnejša Maier-Saupejev mikroskopski opis [9] in Landau-de Gennesov fenomenološki pristop [10]. Od takrat interes za tekoče kristale ni usahnil, saj ga vzpodbuja tako tehnološki razvoj kot tudi bazične raziskave, ki se v zadnjem obdobju pogosto prepletajo z novimi, izrazito interdisciplinarnimi področji [15], med drugim s fiziko koloidov, biotehnologijo, senzoriko, medicino in aplikacijami kompleksnih kompozitnih materialov v optiki in fotoniki.

Koloidi so disperzije trdnih delcev, kapljic ali plinskih mehurčkov v gostiteljskem mediju, pri čemer je značilna velikost vključkov v območju od nekaj nm do nekaj $10\ \mu\text{m}$. Mednje prištevamo raznovrstne materiale, kot so črnilo, mineralna olja, barve, sirupi in maslo, zato so deležni osrednje pozornosti farmacevtske, prehranske in petrokemične industrije [16]. Koloidna dispergirana faza vpliva na gostiteljski medij z interakcijami preko površine [17]. Površine koloidnih delcev so lahko kemično aktivne ali inertne, električno nabite ali nenabite oziroma pokrite s površinskim slojem (surfaktantom), ki vsiljuje različna površinska polja. Najpogostejša površinska sila je van der Waalsova sila, ki ima dielektrični izvor in jo povzroča fluktuiranje porazdelitve naboja

v atomih ali molekulah. Elektrostatične sile Coulombskega izvora delujejo v koloidnih disperzijah z ionizirabilno kontinuumsko fazo ali ob prisotnosti nabitih delcev [18]. Volumske sile so pomembne v koloidnih disperzijah, ki so izpostavljene zunanjim poljem (električno, magnetno, gravitacijsko) ali v materialih s feroelektričnimi oziroma feromagnetnimi lastnostmi.

Tekočerkristalni koloidi predstavljajo novo vrsto mehke snovi, ki je v zadnjem desetletju pritegnila precejšnjo pozornost svetovne raziskovalne sfere [19–21]. Nenehne zahteve po vedno bolj kompleksnih mehanskih in optičnih odzivih tako tekočerkristalnih kot koloidnih komponent so privedle do sinergije obeh področij v novem tipu materialov, ki ponujajo zanimive aplikacije v obliki prilagodljivih elektro-optičnih elementov, svetlobnih vodnikov in senzorjev. Koloidni delci, dispergirani v tekočem kristalu, vzajemno vplivajo na urejenost tekočega kristala preko površinskega sidranja [22]. Površine delcev so praviloma pokrite s površinskim slojem, ki vsiljuje pravokotno (homeotropno), nagnjeno ali ravninsko (planarno) urejanje tekočerkristalnih molekul ob površini. Površinsko urejanje vpliva na tekoči kristal preko ustvarjanja elastične deformacije direktorskega polja v okolici koloidnega delca. Taka motnja v direktorskem polju ima dipolno ali kvadrupolno simetrijo, zato kombinacijo delcev, okoliške motnje in morebitnih topoloških defektov pogosto imenujemo elastični dipoli oziroma kvadrupoli [21]. Za elastični dipol sferičnega homeotropnega delca je značilen -1 hiperbolični defekt, ki spremlja delec, za elastični kvadrupol pa $-\frac{1}{2}$ defektni Saturnov obroč, ki obkroža delec v ravnini ekvatorja [23]. Delci s planarnim površinskim sidranjem imajo vedno kvadrupolno simetrijo direktorja z dvema površinskima $-\frac{1}{2}$ 'boojum' defektoma. Simetrijo in strukturo direktorskega polja okrog koloidnih delcev določajo predvsem jakost površinskega sidranja, velikost delcev, ograjenost z mejnimi površinami in zunanja polja [21]. Slika 1 prikazuje mikroskopske posnetke in shematsko konfiguracijo elastičnega dipola in kvadrupola ter vpliv fizikalnih parametrov na direktorsko strukturo.



Slika 1: (a) Dipolna in (b,c) kvadrupolna konfiguracija direktorskega polja okrog homeotropnega delca. Direktorsko polje je prikazano s črnimi črtami. Z manjšanjem delca in jakosti sidranja ali z večanjem zunanjega polja in ograjenosti postane dipolna struktura energijsko manj ugodna, zato se preoblikuje v kvadrupolno. Mikroskopski posnetki vzorcev se lepo skladajo s teoretično predstavitvijo. Povzeto po sliki 12 v referenci [21].

Med delci v tekočem kristalu delujejo strukturne sile dolgega dosega. Te sile so termodinamičnega tipa, njihov izvor pa predstavljajo van der Waalove medmolekulske interakcije na molekularni skali. Na skali delcev se prispevki posameznih molekul zabrišejo, tako da tekoči kristal učinkovito deluje kot elastični medij, ki poskuša ohranяти orientacijski red lastnih molekul. Strukturne sile tako igrajo vlogo učinkovitih elastičnih sil, ki minimizirajo elastično motnjo in prenašajo napore v direktorskem polju, ki jih povzročajo dispergirani delci. Prostorska odvisnost strukturnih

sil je tipično močno anizotropna in je določena z geometrijo sistema in simetrijo direktorja. Kompleksne interakcije med koloidnimi delci v tekočem kristalu so zato odgovorne za nastanek različnih koloidnih struktur.

Pojav asistiranega in spontanega samosestavljanja je bil v zadnjih letih odkrit in raziskan v različnih tekočokristalnih koloidnih disperzijah [20,25,26]. V začetni fazi eksperimentov so opazili verige elastičnih dipolov pri prikazu lokov (*arceaux*) z dekoracijsko tehniko v kapljicah holesteričnega tekočega kristala [8,27]. Strukturo dipolnih linearnih verig so dokončno prepoznali in razumeli Poulin in sodelavci [19,28] v večkratnih emulzijah vodnih kapljic znotraj nematskih kapljic. Sestavljanje dipolnih verig v večjem obsegu je bilo omogočeno s fazno separacijo v binarnih mešanicah silikonskega olja in nematskega tekočega kristala [29]. Posamezni segmenti dipolnih verig lahko tvorijo dvodimenzionalne (2D) gruče [24], medtem ko se kvadrupolni delci v nematiku spontano uredijo v nazobčane verige [30]. Šele pred kratkim smo uspeli urediti koloidne delce v pravilne 2D nematske koloidne kristale [31,32,80,81]. Na meji dveh tekočin so opazili 2D heksagonalno urejanje kapljic glicerola in steklenih kroglic [37–43]. Odkrili so tudi: z delci povezane holesterične gele [44,45], orientacijsko urejanje feromagnetnih nanožičk v anizotropni tekočini [46–48], kombinirano elektrostatično-nematsko stabilizacijo koloidnih disperzij [49] in različne tipe meddelčnih potencialov v nematiku [50–53].

Glavna motivacija za raziskave tekočokristalnih koloidov je razvoj novih optičnih elementov, fotonских struktur in metamaterialov [54–57]. Tridimenzionalni (3D) fotonски kristali [58–60], resonatorji z deljenim nihajnim krogom [61], metamateriali v območju infrardeče svetlobe [62–65] in superleče z negativnim lomnim količnikom [66–69] namreč zahtevajo dobro kontrolo dielektričnosti in magnetne permeabilnosti na mikrometrski skali. Dejstvo je, da lahko odziv tekočokristalnih koloidov na tej velikostni skali razmeroma enostavno nadzorujemo s primernim izborom delcev, obdelavo njihovih površin in urejanjem pod vplivom zunanjih polj [70–72]. Uporabne so tudi metode samosestavljanja, ki še posebej zanimajo proizvajalce kompozitnih materialov [31,76,77]. V primerjavi s koloidnimi sistemi na osnovi izotropnega gostiteljskega medija, kot je npr. voda, so vezavne energije med delci v tekočem kristalu mnogo večje [78–82] in dosegaajo nekaj $1000\ k_B T$ ali celo $10000\ k_B T$ v primeru prepletenih koloidnih struktur [83–85]. Vezavne energije v elektrostatično stabiliziranih koloidih z vodo kot gostiteljskim medijem namreč dosegaajo zgolj $10\ k_B T$ [86,87]. Mehanizem sestavljanja delcev s strukturnimi silami v tekočokristalnih koloidih omogoča tudi skaliranje velikosti delcev v nanometrsko območje [88,89], kar postavlja potencialne optične aplikacije globoko v območje UV svetlobe. Nedavno so tudi pokazali, da dopiranje nematskih mešanic s kemijsko funkcionaliziranimi nanodelci občutno pospeši elektrooptični odziv in močno razširi temperaturno stabilnost holesteričnih modrih faz [90–95].

Doktorsko delo obravnava meddelčne interakcije in sestavljanje koloidnih struktur v tankih plasteh nematskega tekočega kristala z uporabo optične pincete. Natančneje raziščemo lastnosti meddelčnih interakcijskih potencialov, (meta)stabilnost koloidnih struktur v različnih geometrijah, vpliv inducirane nereda na defekte v koloidnih strukturah, gradnjo 2D koloidnih kristalov v planarnem in kiralnem nematskem polju, stabilizacijo urejenih struktur v zunanjem električnem polju, vpliv oblike delcev na interakcije in nastanek topoloških defektov, vezavo delcev s pobeglimi defektnimi obroči in kompleksno prepletanje defektnih linij v obliki vozlov in zank. Čeprav je delo v celoti eksperimentalno, je ves čas potekalo vzporedno s teoretično obravnavo problemov, zato predstavlja komplement in neodvisno potrditev mnogih hipotez o sestavljanju koloidnih delcev v anizotropnih tekočinah. Glavni del doktorskega dela obravnava pobege in prepletene 2D koloidne strukture v kiralnem nematskem polju, ki predstavljajo nov način stabilizacije kompleksnih topoloških objektov. Koloidni delci so vezani z delokaliziranimi defektnimi linijami v neločljivo povezane topološke objekte, ki imajo zanimive lastnosti. Mednje spadajo kiralnost, močan strunast meddelčni potencial in možnost spreminjanja topologije. Najveličastnejši dosežek predstavlja odkritje vozlov in zank iz defektnih linij, ki jih spretno prepletamo okrog urejenih koloidnih delcev. Poudariti velja, da je bilo začetno obdobje raziskav osredotočeno na pridobivanje izkušenj, učenje eksperimentalnih metod in teoretičnih konceptov, medtem ko je

nadaljevanje prineslo mnogo neodvisnih idej, ki so privedle do uspešne realizacije in nadgradnje predhodnih dosežkov. Rezultati doktorskega dela so bili večinoma že predstavljeni strokovni javnosti v obliki raznih znanstvenih prispevkov [31,35,80–83,96,97].

Teoretično ozadje

Landau-de Gennesov model proste energije

Orientacijsko urejanje nematskega tekočega kristala fenomenološko opišemo s simetričnim brez-slednim *tenzorjem ureditvenega parametra* $\mathbb{Q}$. Uvedemo ga z izrazom

$$\mathbb{Q} = \frac{1}{2}S(3\mathbf{n} \otimes \mathbf{n} - \mathbb{I}) + \frac{1}{2}\mathcal{B}(\mathbf{e}_1 \otimes \mathbf{e}_1 - \mathbf{e}_2 \otimes \mathbf{e}_2), \quad (6.1)$$

pri čemer je $\mathbf{n}$ direktor, $S \in [-\frac{1}{2}, 1]$ je *skalarni ureditveni parameter*, $\mathcal{B} \in [-\frac{3}{2}, \frac{3}{2}]$ je *biaksialnost* oziroma *dvoosnost*, $\mathbf{e}_1$ je sekundarni direktor in $\mathbf{e}_2 = \mathbf{n} \times \mathbf{e}_1$. Stopnjo nematskega reda S določa jakost fluktuacij molekulskih orientacij okrog direktorja. Formalno je S definiran kot ansambelsko povprečje drugega Legendrovega polinoma, pomnoženega s skalarnim produktom med orientacijami posameznih molekul in direktorjem. Dvoosnost $\mathcal{B}$ opisuje odstopanje nematskega reda od enoosne ureditve, ki se lahko pojavi na površinah ali pod vplivom zunanjih polj. Sekundarni direktor podaja smer dvoosnega urejanja. Tenzor $\mathbb{Q}$ v celoti vključuje pet prostostnih stopenj nematskega orientacijskega reda: orientacijo direktorja (dva kota), orientacijo sekundarnega direktorja glede na direktor (en kot), stopnjo nematskega reda in dvoosnost. V diagonalni obliki ima $\mathbb{Q}$ tri različne lastne vrednosti, S , $-\frac{1}{2}(S + \mathcal{B})$ in $-\frac{1}{2}(S - \mathcal{B})$ ter pripadajoče lastne vektorje $\mathbf{n}$, $\mathbf{e}_1$ in $\mathbf{e}_2$.

Stabilnost nematske mezofaze je pri večini tekočerkristalnih materialov odvisna od temperature ali koncentracije. Obravnavali bomo termotropne tekoče kristale, kjer temperatura določa, ali so nematske molekule v izotropni, nematski, smektični ali steklasti mezofazi. Temperatura je tudi glavni parameter, ki sproži prehod med različnimi mezofazami. Fazni prehod med izotropno in nematsko fazo, ki ga uporabimo za tvorbo prepletenih defektov je *nezvezen* oziroma prvega reda. Latentna toplota tipičnega tekočega kristala 5CB je 1560 J/kg [99], temperatura prehoda med nematsko in izotropno fazo pa 308.4 K.

Uveljavljen pristop k opisu nematsko-izotropnega (N-I) faznega prehoda je tvorba funkcionala proste energije preko Landauovega razvoja skalarnih invariant tenzorja nematskega ureditvenega parametra. Osnovna gostota proste energije f_{ORD} , ki je potrebna za opis N-I prehoda, je četrtega reda v $\mathbb{Q}$ in se zapiše kot [8]:

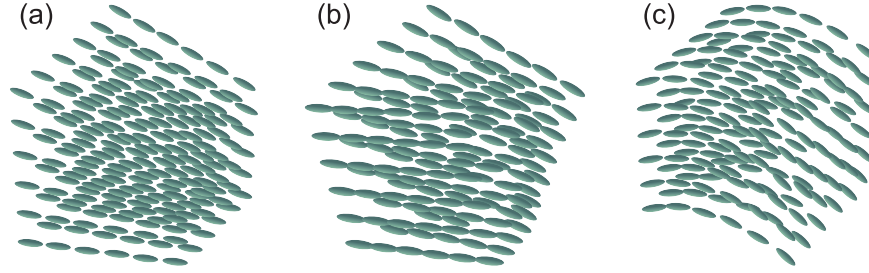
$$f_{ORD} = \frac{1}{2}a(T - T_{NI}^*)\text{tr}\mathbb{Q}^2 + \frac{1}{3}B\text{tr}\mathbb{Q}^3 + \frac{1}{4}C(\text{tr}\mathbb{Q}^2)^2, \quad (6.2)$$

pri čemer so a , B , in C fenomenološki materialni parametri, T je temperatura in T_{NI}^* je najnižja možna temperatura podhlajene izotropne faze. Tipične vrednosti materialnih parametrov so: $a \sim 10^5$ J/m³K, $B \sim -10^6$ J/m³ in $C \sim 10^6$ J/m³. V nematski fazi sta tako predfaktorja prvih dveh členov v razvoju negativna in edino $C > 0$ zagotavlja omejenost funkcionala gostote proste energije navzdol. Parameter $a(T - T_{NI}^*)$ je temperaturno odvisen in sproži N-I prehod.

Nematik se obnaša kot efektivno elastičen medij, če mu vsilimo prostorsko nehomogeno orientacijsko urejanje. Vsako elastično deformacijo lahko sestavimo iz treh osnovnih elastičnih deformacijskih načinov: pahljačnega, zvojnega in upogibnega, ki so prikazani na sliki 2. Fenomenološko se elastičnost nematika opiše z generaliziranimi prostorskimi odvodi tenzorja nematskega ureditvenega parametra, s katerimi konstruiramo gostoto elastične proste energije f_E . Splošno uporabljana de Gennesova formulacija gostote elastične proste energije se zapiše kot [8,100]:

$$f_E = \frac{1}{2}L_1 \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k} + \frac{1}{2}L_2 \frac{\partial Q_{ij}}{\partial x_j} \frac{\partial Q_{ik}}{\partial x_k} + \frac{1}{2}L_3 Q_{ij} \frac{\partial Q_{kl}}{\partial x_i} \frac{\partial Q_{kl}}{\partial x_j}, \quad (6.3)$$

pri čemer so L_1 , L_2 in L_3 tenzorske elastične konstante ter x_i kartezične koordinate; v zapisu velja seštevanje po ponovljenih indeksih. Tri elastične konstante opišejo tri osnovne elastične načine. Konstante L_i niso odvisne od stopnje nematske urejenosti in jih lahko interpretiramo kot neposredno jakost medmolekulskih interakcij.



Slika 2: Osnovni elastični deformacijski načini: (a) pahljača, (b) zvoj in (c) upogib.

Gostoto elastične proste energije f_E lahko prepišemo iz tenzorske oblike v direktorsko, če predpostavimo enoosno urejanje nematika [101]. Tenzor ureditvenega parametra naj bo enoosen, $\mathbb{Q}^U = \frac{1}{2}S(3\mathbf{n} \otimes \mathbf{n} - \mathbb{I})$, ob uporabi zvez $\mathbf{n} \cdot \mathbf{n} = 1$ in $n_i(\partial n_i)/(\partial x_k) = 0$ pa lahko elastično prosto energijo zapišemo v standardni Frank-Oseenovi obliki:

$$f_E^{FO} = \frac{1}{2}K_{11}(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_{22}[\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + \frac{1}{2}K_{33}[\mathbf{n} \times (\nabla \times \mathbf{n})]^2, \quad (6.4)$$

kjer so Frankove elastične konstante K_{ii} podane s konstantami L_i [100]: $L_1 = (K_{33} + 2K_{22} - K_{11})/(9S^2)$, $L_2 = 4(K_{11} - K_{22})/(9S^2)$ in $L_3 = 2(K_{33} - K_{11})/(9S^3)$. Konstante K_{ii} vključujejo stopnjo nematske urejenosti S kot notranji parameter in so sorazmerne S^2 . Prednost uporabe nabora konstant K_{ii} je v neposredni povezavi s pripisanim osnovnim elastičnim deformacijskim načinom: K_{11} karakterizira pahljačni, K_{22} zvojni in K_{33} upogibni elastični način.

Gostoti elastične proste energije, opisani z enačbama (6.3) in (6.4), sta zapletena prostorska funkcionala, v kolikor ju uporabljamo z vsemi tremi elastičnimi konstantami. Zato se pogosto uporabi približek ene elastične konstante, pri čemer velja $L_1 = L$, $L_2 = L_3 = 0$ in $K_{11} = K_{22} = K_{33} = K$. Gostoti prostih energij f_E in f_E^{FO} se v tem približku zapišeta kot:

$$f_E = \frac{1}{2}L \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k}, \quad (6.5)$$

$$f_E^{FO} = \frac{1}{2}K [(\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2]. \quad (6.6)$$

Primernost uporabe približka ene elastične konstante je močno odvisna od izbranega materiala. V nematskem tekočem kristalu 5CB konstante K_{ii} odstopajo od povprečne vrednosti $6 \cdot 10^{-12}$ N za največ 40 % [105].

Gostota elastične proste energije f_E in gostota proste energije nematske urejenosti f_{ORD} skupaj sestavljata Landau-de Gennesov (LdG) model proste energije, ki predstavlja osnovni model za fenomenološki opis nematika. Gostota proste energije f_{LdG} se tako zapiše kot:

$$f_{LdG} = f_E + f_{ORD}. \quad (6.7)$$

Landau-de Gennesov model ustrezno opiše orientacijsko urejanje nematskega tekočega kristala na mikrometrski skali, saj vključuje oba osnovna mehanizma: nematsko elastičnost in možnost variacij stopnje nematskega reda. Uporabi se lahko na poljubnih geometrijah, različnih velikostnih skalah in je preprosto razširljiv za opis vplivov zunanjih polj. Edina svojstvena omejitev LdG modela je, da postane manj zanesljiv na nanometrski skali, saj se tenzor ureditvenega parametra, na katerem temelji LdG model, uvede kot povprečno molekularno polje. Razmerje med velikostjo gostot elastične proste energije f_E in energije nematskega reda f_{ORD} uvede v LdG model karakteristično dolžino, imenovano *nematska korelacijska dolžina* ξ_N :

$$\xi_N = \sqrt{\frac{L}{a(T - T_{NI}^*) + BS_{eq} + \frac{9}{2}CS_{eq}}}. \quad (6.8)$$

kjer je $S_{eq} = -\frac{B}{6C} + \frac{1}{2}\sqrt{(\frac{B}{3C})^2 - \frac{8a}{3C}(T - T_{NI}^*)}$ ravnovesna velikost stopnje nematske urejenosti v orientacijsko homogenem vzorcu. Fizikalna interpretacija ξ_N ustreza določanju prostorske skale spreminjanja stopnje nematskega reda. V nematiku se njena vloga izrazi predvsem v defektihi, saj v grobem določa njihovo velikost in tipično meri nekaj nm.

Površinsko sidranje

Interakcija tekočega kristala s trdno, tekočo ali plinasto mejno plastjo vsiljuje na površini preferenčno stopnjo nematskega reda in preferenčno orientacijo tekočerkristalnih molekul. Ta pojav imenujemo *površinsko sidranje* [22], ki je lahko uniformno, če obstaja ena sama preferenčna os orientacije nematika, lahko pa je degenerirano, če sta določena zgolj stožec ali ravnina preferenčnih osi. Uniformno površinsko sidranje opišemo s funkcionalom površinske gostote proste energije f_s^{uni} [8]:

$$f_s^{uni} = \frac{1}{2}W_e^{uni}\text{tr}(\mathbb{Q} - \mathbb{Q}_0)^2, \quad (6.9)$$

pri čemer je W_e^{uni} uniformna jakost sidranja in $\mathbb{Q}_0$ tenzor ureditvenega parametra, vsiljen s površino. Površinska gostota proste energije f_s^{uni} kvadratično omejuje odstopanje $\mathbb{Q}$ od $\mathbb{Q}_0$ in določa tako preferenčno os kot tudi stopnjo nematskega reda na površini. Tipične vrednosti W_e^{uni} so med 10^{-3} J/m² in 10^{-7} J/m² [109]. Moč uniformnega površinskega sidranja lahko zapišemo tudi v obliki Kleman-de Gennesove *ekstrapolacijske dolžine* ξ_S [8,110], definirane z enačbo $\xi_S = K/W_e^{uni}$, pri čemer je K efektivna Frankova elastična konstanta. Za tipični nematik ($K \sim 10^{-11}$ N), ograjen z močnim površinskim sidranjem ($W_e^{uni} \sim 10^{-3}$ J/m²), znaša ξ_S nekaj 10 nm, medtem ko v primeru šibkega sidranja ($W_e^{uni} \sim 10^{-6}$ J/m²) doseže tudi 10 μ m [111].

Vpliv zunanega električnega polja

Obstajajo štiri osnovne interakcije med zunanjim električnim poljem in tekočim kristalom: (i) dielektrična, (ii) fleksoelektrična, (iii) zaradi polarizacije površine, ki je posledica naelektrenih mejnih plasti in (iv) zaradi gibanja nabitih delcev. Osredotočimo se na dielektrično interakcijo in zanemarimo ostale vplive. Zunanje električno polje deluje na nepolarni nematik preko dielektrične interakcije z induciranimi dipoli tekočerkristalnih molekul. Glede na polarizabilnost molekul se inducirani dipoli orientirajo vzporedno ali pravokotno na direktor. V okviru Landau-de Gennesovega modela se dielektrična sklopitev med električnim poljem in nematikom uvede kot dodaten člen v gostoti proste energije f_e [100]:

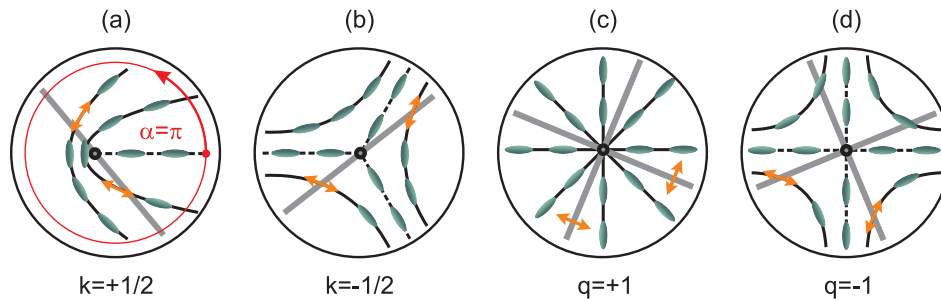
$$f_e = -\frac{1}{2}\epsilon_0\left(\bar{\epsilon}E_i^2 + \frac{2}{3}\epsilon_a^{mol}Q_{ij}E_iE_j\right), \quad (6.10)$$

kjer je ϵ_0 dielektrična konstanta, $\bar{\epsilon} = \frac{1}{3}(2\epsilon_{\perp} + \epsilon_{\parallel})$ povprečna dielektričnost tekočega kristala, $\epsilon_a^{mol} = \epsilon_{\parallel}^{mol} - \epsilon_{\perp}^{mol}$ molekularna dielektrična anizotropija in E_i jakost električnega polja v i -ti smeri. $\epsilon_{\perp}^{mol}$ in $\epsilon_{\parallel}^{mol}$ sta lastni vrednosti tenzorja molekularne dielektrične konstante, ki ustrezata pravokotni in vzporedni orientaciji glede na direktor. Molekularna dielektričnost ϵ_a^{mol} in makroskopska dielektričnost ϵ_a sta povezani preko skalarne ureditvenega parametra S z enačbo $\epsilon_a = S\epsilon_a^{mol}$. Relativen vpliv električnega polja opiše *električna koherentna dolžina* ξ_E , ki jo uvedemo z izrazom $\xi_E = \sqrt{K/\epsilon_0\epsilon_aE^2}$ [8]. ξ_E podaja razmerje med reorientacijskimi efekti, povzročenimi z nematsko elastičnostjo in reorientacijo kot posledico električnega polja. Za tipični nematik v električnem polju $E = 1$ V/ μ m znaša $\xi_E \sim 0.3$ μ m.

Topologija nematskih defektov

Topološki defekti [120–122] so nujna posledica zlomljene simetrije in se pojavljajo v raznovrstnih fizikalnih sistemih, med drugim v supertekočem heliju³He [123], kristalih, tekočih kristalih [124] in kvantnih tekočinah [125]. Imajo ključno vlogo pri razumevanju odziva snovi na zunanje obremenitve, v bližini faznih prehodov [126], pri relaksaciji snovi v ravnovesno stanje [127] in celo pri študiju nekaterih kozmoloških modelov [128].

Defekti v orientacijskem redu tekočega kristala so posledica frustriranih orientacij molekul, povzročenih z ograjenostjo. Nasprotujoče preferenčne orientacije na površinah povzročijo tvorbo območij, v katerih molekule izgubijo orientacijski red in so podvržene močnim prostorskim fluktuacijam. Defekti v nematskem tekočem kristalu so bodisi linije bodisi točke [104,129]. V okviru topologije se linijskim defektom pripiše *ovojno število*, točkovnim defektom pa *topološki naboj* [121,129]. Zaključene defektne linije v obliki zank so topološko ekvivalentne točkovnim defektom. Nekaj osnovnih primerov je prikazanih na sliki 3.



Slika 3: Konfiguracije direktorskega polja v bližini topoloških defektov z različno močjo. (a,b) Defektna linija z ovojnim številom $\frac{1}{2}$ in $-\frac{1}{2}$ so predstavljene s črnimi sklenjenimi črtami, ki ponazarjajo geometrijsko ureditev molekul. (c,d) Točkasta defekta s topološkim nabojem $+1$ oziroma -1 . Sive črte ponazarjajo območja sipane svetlobe, ko tekočokristalni vzorec opazujemo med prekrizanimi polarizatorjema. Položaj polarizatorjev je nakazan z oranžnima puščicama, smer obhoda molekul pa z rdečo puščico [8].

Ovojno število disklinacijske linije k opiše lokalno simetrijo okoliškega direktorskega polja. Uvede se kot razmerje $k = \frac{\alpha}{2\pi}$, kjer je α kot zasuka direktorja pri obhodu disklinacijske linije po zaključeni zanki [104]. Geometrijska vloga ovojnega števila se razkrije, če zapišemo direktor okrog defektne linije v obliki $\mathbf{n} = (\cos \frac{\phi}{2}, \sin \frac{\phi}{2}, 0)$, pri čemer leži linija vzdolž smeri z , kot ϕ pa podaja smer direktorja v ravnini. Z minimizacijo proste energije in uporabo hodografskega pravila $\oint d\phi = 2\pi k$ [130] dobimo rešitev Euler-Lagrangeove enačbe $\nabla^2 \phi = 0$:

$$\phi = k\theta + c(r, \theta), \quad (6.11)$$

kjer je c običajno konstanta, ki določa relativno orientacijo disklinacijske linije glede na koordinatno izhodišče. Energija disklinacijske linije je sorazmerna s k^2 in se zapiše kot:

$$W_{DL} = \pi K k^2 \ln \frac{R}{r_c} + W_c, \quad (6.12)$$

pri čemer r_c ustreza polmeru jedra defekta, R velikosti sistema in W_c energiji jedra defekta na enoto dolžine. Sorazmerje $W_{DL} \propto k^2$ v enačbi (6.12) pokaže, da sta energijsko stabilni zgolj disklinacijski liniji z ovojnim številom $\frac{1}{2}$ oziroma $-\frac{1}{2}$ [124].

Topološki naboj točkovnega defekta q se uvede kot integral preko sklenjene površine, ki obkroža defekt [129,130,138]:

$$q = \frac{1}{8\pi} \oint_{\sigma} \epsilon_{ijk} \mathbf{n} \cdot \left(\frac{\partial \mathbf{n}}{\partial x_j} \times \frac{\partial \mathbf{n}}{\partial x_k} \right) dS_i, \quad (6.13)$$

kjer je ϵ_{ijk} Levi-Civitàjev popolnoma antisimetrični tenzor in kjer x_i predstavlja kartezične koordinate. Enačba (6.13) je liha v $\mathbf{n}$, kar onemogoča nedvoumno definicijo predznaka topološkega

naboja zaradi $\mathbf{n} \rightarrow -\mathbf{n}$ simetrije. Pri tem mora biti površina, ki obkroža obravnavan defekt, sama brez defektov.

V okviru topologije je topološki naboj preslikava direktorskega polja Σ iz zaključene površine σ v prostor ureditvenega parametra, ki je v tem primeru enotska krogla S^2 [104]. Če Σ pokrije S^2 le delno, je konfiguracija defektov znotraj σ topološko nestabilna in ekvivalentna uniformnemu polju. Tako preslikavo lahko skrčimo v točko. Preslikave Σ , ki pokrije celotno enotsko sfero prostora ureditvenega parametra, se ne da skrčiti v točko, zato predstavlja topološko stabilen točkovni defekt. Število, ki pove kolikokrat Σ pokrije enotsko sfero, je enako topološkemu naboju. Vrednosti q so celoštevilске in ustrezajo $0, \pm 1, \pm 2, \dots$. Topološke invariante se pri nastajanju in izničenju defektov ohranjajo. Ob vsakem vnosu defekta se v sistemu pojavi nasproten defekt, ki kompenzira motnjo prvega. Celotno ovojno število dveh defektnih linij, ki imata ovojni števili nasprotnih predznakov, je enako nič: $-\frac{1}{2} + \frac{1}{2} = 0$. Če dve taki defektni liniji nastaneta, se privlačita in se ob stiku izničita, pri čemer nastane konfiguracija nematika z ovojnim številom enakim nič. Podobno velja tudi za točkovna defekta z nasprotnima topološkima nabojema, ki se prav tako privlačita in na koncu izničita: $-1 + 1 = 0$. Poudariti velja, da je potrebno topološka pravila za seštevanje ovojnega števila in topološkega naboja uvesti v skladu z dogovorom o predznaku ovojnega števila in topološkega naboja. Celotno ovojno število k_t oziroma celoten topološki naboj q_t sta namreč v geometrijah z neuniformnim direktorjem določena s sidranjem na ograjujočih površinah. Homeotropna sferična kapljica ima na primer celoten topološki naboj enak $q_t = 1$ [143].

Koloidni delci so v ograjenem nematskem tekočem kristalu efektivno ekvivalentni točkovnim defektom, pri čemer sidranje na površinah in oblika delcev določata njihov topološki naboj. Sferični delec s homeotropno površino ima topološki naboj $+1$. N takih delcev v uniformni geometriji zato potrebuje za kompenzacijo defekte s celotnim topološkim nabojem $-N$. Splošnost tega pravila dovoljuje kompenzacijo topološkega naboja večih delcev s posameznim defektom večjega topološkega naboja ali pa kompenzacijo z več defekti manjšega topološkega naboja. Ta univerzalnost je ključna za razumevanje prepletenih koloidnih struktur.

Multipolni razvoj in meddelčni potenciali

Direktorja, ki ga ustvari koloidni delec v uniformnem polju, analitično ne moremo določiti zaradi močno nelinearnih Euler-Lagrangevih (EL) enačb, ki določajo nematsko elastičnost. Nelinearnost nematika je najbolj izrazita v bližini delcev, kjer so gradienti direktorskega polja največji. Analitična obravna je mogoča edino v limiti daljnjega polja, torej na večjih razdaljah od delca, kjer so prostorski gradienti direktorja majhni in se EL enačbe lahko linearizirajo. Analitične rešitve lineariziranih EL enačb so elastični multipoli [21,131].

Multipolni razvoj predpostavlja skoraj uniformni direktor $\mathbf{n}(\mathbf{r}) = (n_x, n_y, 1)$, kjer sta $n_x \ll 1$ in $n_y \ll 1$ zgolj majhni motnji. Za tak direktor se Frankova elastična prosta energija f_E^H iz enačbe (6.6) prepiše v:

$$f_E^H = \frac{1}{2}K \sum_{\mu=x,y} (\nabla n_\mu)^2. \quad (6.14)$$

Euler-Lagrangevi enačbi za tako prosto energijo sta Laplaceovi enačbi $\nabla^2 n_\mu = 0$. Za velike oddaljenosti od centra delca r se rešitev Laplaceove enačbe zapiše kot vsota multipolov [131]:

$$n_\mu = \frac{A^\mu}{r} + \frac{\mathbf{p}^\mu \cdot \mathbf{r}}{r^3} + \frac{c_{ij}^\mu x_i x_j}{r^5} + \dots, \quad \mu = x, y, \quad (6.15)$$

kjer so A^μ , $\mathbf{p}^\mu$ in c_{ij}^μ koeficienti v razvoju, x_i pa so kartezične koordinate radij vektorja $\mathbf{r}$. Direktorsko polje okrog delca mora biti invariantno na rotacije okrog osi nemotenega direktorja $\mathbf{n}_0 = (0, 0, 1)$, kar postavi $A^\mu = 0$. Ob upoštevanju dipolne in kvadrupolne simetrije, rotacijske invariantnosti in uporabi dimenzijske analize se n_μ v multipolni sliki zapiše kot:

$$n_\mu = p_z \frac{\mu}{r^3} + 2c \frac{z\mu}{r^5}, \quad \mu = x, y. \quad (6.16)$$

kjer za momenta p_z in c veljata sorazmerji $p_z \propto d^2$ in $c \propto d^3$, pri čemer je d premer delca.

Meddelčni potencial lahko določimo analitično z uporabo multipolnega razvoja. Interakcija temelji na prekrivanju deformacijskih območij daljnega direktorskega polja. Elastični potencial $U(\mathbf{R})$ med dvema delcema na položajih $\mathbf{r}$ in $\mathbf{r}'$ ($\mathbf{R} = \mathbf{r} - \mathbf{r}'$), z dipolnima in kvadrupolnima momentoma p, p' in c, c' ustreza [21]:

$$U(\mathbf{R}) = 4\pi K \left[pp'V_{PP}(\mathbf{R}) + \frac{4}{9}cc'V_{CC}(\mathbf{R}) + \frac{2}{3}(cp' - c'p)V_{PC}(\mathbf{R}) \right], \quad (6.17)$$

pri čemer so interakcijski členi določeni z:

$$V_{PP}(\mathbf{r}) = \frac{1}{r^3}(1 - 3\cos^2\theta), \quad (6.18)$$

$$V_{CC}(\mathbf{r}) = \frac{1}{r^5}(9 - 90\cos^2\theta + 105\cos^4\theta), \quad (6.19)$$

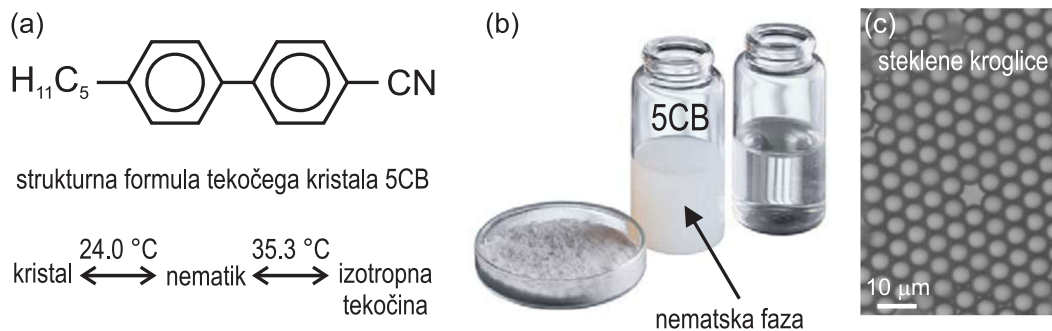
$$V_{PC}(\mathbf{r}) = \frac{1}{r^4}(15\cos^3\theta - 9\cos\theta), \quad (6.20)$$

in θ predstavlja kot med $\mathbf{R}$ in $\mathbf{n}_0$. Kompaktna oblika meddelčnega potenciala v enačbi (6.17) temelji na naslednjih predpostavkah in poenostavitvah: (i) direktor je skorajda uniformen $\mathbf{n} = (n_x, n_y, 1)$; $n_x, n_y \ll 1$, (ii) delci interagirajo v neskončnem nematskem mediju, (iii) delci posedujejo samo elastične dipole in kvadrupole, (iv) razmik med delci je dovolj velik, da direktor ohrani dipolen oziroma kvadrupolen profil. Poenostavitvam navkljub, eksperimenti kvalitativno potrjujejo prostorsko in potenčno odvisnost zapisanih meddelčnih potencialov [33,52,78,136].

Materiali in eksperimentalne metode

Opis in priprava vzorcev

V eksperimentih smo uporabljali termotropni monomerni tekoči kristal 4-ciano-4'-pentil-bifenil, znan pod imenom 5CB. Tvorijo ga podolgovate organske molekule s togo hrbtenico iz benzenovih obročev, na katero so pripete gibljive alkilne verige in močno polarne CN glave, ki zagotavljajo dielektrično anizotropijo in dipolni privlak med molekulami. Pri nizkih temperaturah je 5CB bel prah, sestavljen iz drobnih kristalčkov. Ko ga segrejemo do 24 °C, se stali in preide v tekočerkristalno nematsko fazo, tej pa nad 35 °C sledi bistra in prozorna izotropna faza (slika 4).



Slika 4: (a) Strukturna formula tekočega kristala 5CB. Molekula je sestavljena iz toge nepolarne verige ogljikovodikov, dveh benzenovih obročev in polarne CN glave. (b) Vzorec 5CB v kristalni, nematski in izotropni fazi [183]. (c) Vzorec steklenih koloidnih kroglic velikosti 5 μm .

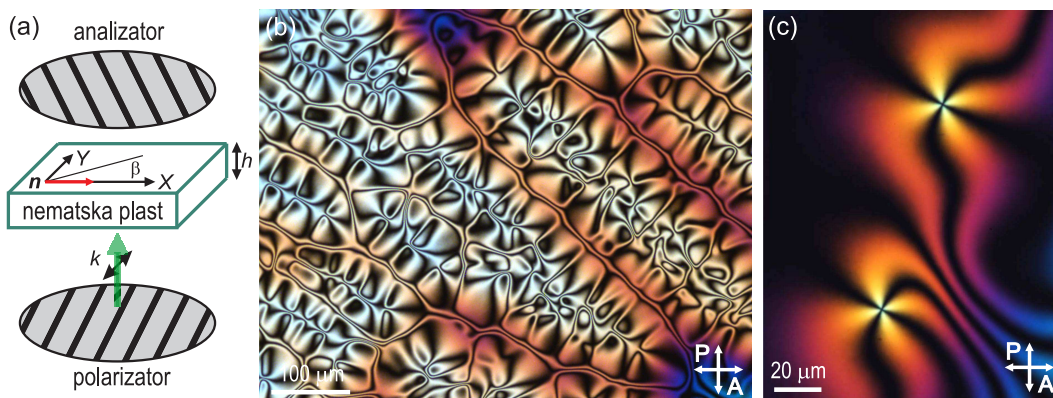
Tekočemu kristalu smo običajno primešali steklene koloidne kroglice velikosti nekaj μm , ki so dobro vidne pod optičnim mikroskopom. Površina kroglic je bila naprej obdana s tankim slojem surfaktanta N,N-dimetil-N-octadecil-3-aminopropil-trimetoksilil klorid (DMOAP silan), ki zagotavlja močno sidranje tekočerkristalnih molekul pravokotno na površino koloidnih delcev. Tako

pripravljene tekočerkristalne koloidne disperzije smo študirali v ograjeni geometriji tekočerkristalnih celic z dobro definiranimi površinami pri sobni temperaturi. Uporabljali smo predvsem tanke planarne, homeotropne in zasukane (twist) nematske celice, kjer je zaželeno, da površina čimbolj vsiljuje določeno orientacijo tekočega kristala.

Običajno uredimo tekoče kristale tako, da jih naneseemo na očiščeno, homogeno in ustrezno pripravljeno površino stekla. Če želimo doseči planarno orientacijo molekul, kjer leži direktor v ravnini substrata, prevlečemo površino s tankim slojem stabilnega polimera (navadno najlonom ali poliimidom), ki ga potem mehansko podrgnemo z mehko bombažno tkanino in s tem na substratu ustvarimo preferenčno smer. Če pa želimo, da so molekule usmerjene pravokotno na površino, moramo na to površino pripeti relativno dolge molekule surfaktanta (DMOAP silan), med katerimi je ravno dovolj prostora, da se mednje vrinejo manjše podolgovate molekule tekočega kristala. Za študij strukturnih in faznih prehodov imamo na steklu naparjeno še tanko plast prevodnega indij-kositrovega oksida (ITO), ki omogoča aplikacijo zunanega električnega polja in lokalno segrevanje vzorca z močno fokusiranim laserskim snopom. Debelino tekočerkristalnih celic kontroliramo z uporabo nekaj μm debelih metaliziranih polietilenskih folij in jo natančno izmerimo s standardno interferenčno tehniko. Celice napolnimo s pomočjo kapilarnega vleka neposredno pred začetkom eksperimenta.

Optična polarizacijska mikroskopija

Optična mikroskopija omogoča opazovanje, snemanje in nadaljno obdelavo posnetih vzorcev na mikrometrski velikostni skali. Metode optične polarizacijske mikroskopije spadajo med najstarejše eksperimentalne tehnike za proučevanje tekočih kristalov, saj omogočajo opazovanje anizotropije lomnega količnika in razlago simetrijskih lastnosti defektnih struktur v polarizirani svetlobi. Pogosto opazujemo tanke nematske plasti v tekočerkristalni celici, kjer se direktor $\mathbf{n}$ ponekod zvezno in ponekod nezvezno spreminja. Mikroskopska slika ima zato različno svetla in različno obarvana območja, ki včasih tvorijo splet prelivajočih se interferenčnih vzorcev (slika 5). Temne lise opazimo na mestih, kjer je direktor $\mathbf{n}$ vzporeden ali pravokoten na polarizacijo vpadle svetlobe oziroma kjer se smer urejenosti nezvezno spreminja. To se praviloma dogaja v bližnji okolici linijskih in točkovnih defektov, ki jih zato enostavno in hitro opazimo.



Slika 5: (a) Razširjanje svetlobe skozi polarizator, tanko plast nematskega tekočega kristala in analizator. (b) Zanimive interferenčne vzorce lahko opazujemo pri urejanju tanke nematske plasti na površini glicerola. (c) Primer urejenosti tekočerkristalnih molekul v okolici topoloških točkovnih defektov na površini glicerola [5]. Interferenčne barve predstavljajo odklon molekul od optične osi, ki je vzporedna polarizatorju ali analizatorju.

Optična dvolomnost je najvidnejša posledica orientacijske urejenosti tekočih kristalov. Tekočerkristalne molekule so v nematski fazi zaradi oblike in medsebojnih interakcij običajno poravnane vzdolž dolgih molekulskih osi, kar povzroča anizotropno porazdelitev električnih nabojev znotraj posameznih molekul. Sile, ki vežejo te naboje, so v različnih smereh različne, zato odziv

tekočerkristalnega medija na elektromagnetno valovanje karakteriziramo z dielektričnim tenzorjem $\underline{\epsilon}$. Posledično sta tudi hitrost svetlobe c_0 in z njo povezan lomni količnik n odvisna od smeri svetlobnega žarka in od njegove polarizacije.

Svetlobni žarek je sestavni del elektromagnetnega valovanja pri katerem v prostoru nihata jakost električnega polja $\mathbf{E}$ in gostota magnetnega polja $\mathbf{B}$ v medsebojno pravokotnih smereh, obe pa v ravnini, ki je pravokotna na smer razširjanja svetlobe. Opišemo ga z valovnim vektorjem $\mathbf{k}$, ki kaže v smeri razširjanja valovanja, njegova velikost pa je povezana z valovno dolžino svetlobe: $|\mathbf{k}| = \frac{2\pi}{\lambda}$. Polarizacijo svetlobe definiramo z orientacijo vektorja električnega polja, ki ga opišemo v približku ravnega vala: $\mathbf{E}(z, t) = \mathbf{E}_0 \exp[i(kz - \omega t + \varphi)]$. Predpostavili smo, da se valovanje s frekvenco ω in fazo φ širi v z smeri. Če sta valovanji dveh svetlobnih žarkov z enako frekvenco, katerih vektorja električnega polja sta med seboj pravokotna, v fazi ($\Delta\varphi = 0$), je vsota obeh valovanj linearno polarizirana. Če je fazna razlika poljubna, je polarizacija žarka eliptična, saj projekcija vektorja električnega polja na (x, y) ravnino opisuje elipso.

Nematski tekoči kristali so optično anizotropna enosna sredstva, v katerih lokalna smer optične osi sovпада z lokalnim direktorjem $\mathbf{n}$. Optična os je namreč smer, vzdolž katere je hitrost razširjanja elektromagnetnega valovanja neodvisna od polarizacije. Zato se linearno polariziran svetlobni žarek pri prehodu skozi nematsko plast v splošnem razcepi na dva žarka z različnima polarizacijama in hitrostjo razširjanja: *rednega* in *izrednega*. Polarizacija prvega je hkrati pravokotna na optično os in na smer valovnega vektorja $\mathbf{k}$, lomni količnik pa je enak $n_o = \sqrt{\epsilon_{\perp}}$. Polarizacija drugega je pravokotna na $\mathbf{k}$, hkrati pa leži v ravnini, ki jo določata $\mathbf{k}$ in optična os. Ustrezni lomni količnik n_e je odvisen od kota θ med $\mathbf{k}$ in optično osjo, pri čemer velja [104]:

$$\frac{1}{n_e^2} = \frac{\cos^2 \theta}{\epsilon_{\perp}} + \frac{\sin^2 \theta}{\epsilon_{\parallel}}. \quad (6.21)$$

Povsod v zgornjih izrazih označujeta $\epsilon_{\perp}$ in $\epsilon_{\parallel}$ lastni vrednosti diagonaliziranega tenzorja $\underline{\epsilon}$. Redni in izredni žarek potrebujeta za prehod skozi nematsko plast različen čas ($n_o \frac{d}{c_0}$ in $n_e \frac{d}{c_0}$, pri čemer je c_0 hitrost svetlobe v vakuumu), kar se izrazi s fazno razliko valovanj:

$$\Delta\varphi = \frac{2\pi}{\lambda_0}(n_e - n_o)h, \quad (6.22)$$

kjer je λ_0 valovna dolžina svetlobe v vakuumu, $n_e - n_o = \Delta n$ je optična dvolomnost in h debelina nematske plasti. Dvolomnost tekočega kristala 5CB znaša 0.2. Intenziteto prepuščene svetlobe opišemo z enačbo [104]:

$$I = I_0 \sin^2 2\beta \sin^2 \left[\frac{\pi h}{\lambda_0}(n_e - n_o) \right], \quad (6.23)$$

kjer je I_0 intenziteta vhodne svetlobe, β pa kot med optično osjo in vhodnim polarizatorjem. Enačba (6.23) je ključna za razumevanje tekočerkristalnih vzorcev. Fazna razlika in intenziteta sta odvisni od valovne dolžine λ_0 , zato pri opazovanju v beli svetlobi vidimo raznobarvne odtenke. Interferenčne barve so še posebej izrazite v območju $(n_e - n_o)h \approx (1 - 3)\lambda_0$, kar ustreza nekaj μm debeli tekočerkristalni plasti. Očitno je, da bo intenziteta I največja za $\beta = \frac{\pi}{4}$. Eksperimentalne meritve intenzitete prepuščene svetlobe so uporabne za določanje elastičnih konstant tekočega kristala [188] in oceno jakosti sidranja na površinah [109].

Optična pinceta

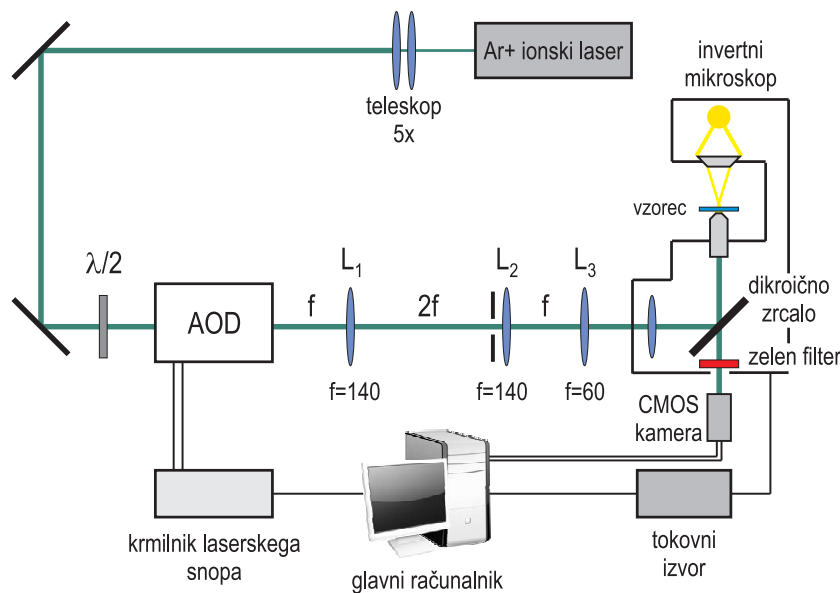
Optična pinceta je naprava, ki s pomočjo močno fokusiranega laserskega snopa omogoča brezkontaktno manipulacijo (pod)mikrometrskih delcev ter meritev sil v območju pikonewtonov. Ashkin je leta 1970 pokazal, da mikrometrške delce z lomnim količnikom, večjim od okoliškega medija, povleče v središče močno fokusiranega laserskega snopa [189]. Od leta 1986, ko so Ashkin, Chu in sodelavci razvili enožarkovno gradientno optično pinceto, ki omogoča ujetje delca v treh dimenzijah in ne samo ob površinah eksperimentalne celice, se tehnika optičnega mikromanipuliranja

nenehno razvija [193]. Danes optično pinceto uporabljajo na mnogih področjih znanosti (pregled v [194–198]), še posebno v molekularni biologiji za neinvazivno manipulacijo celic, celičnih organel, kompleksnih molekul in drugih delcev s podmikrometrsko natančnostjo ter v biofiziki za meritev sil v območju 0.1 – 100 pN [199–204].

Optična past je ustvarjena s fokusiranjem laserskega snopa z mikroskopskim objektivom. Na delec v pasti deluje optična sila, sestavljena iz dveh delov: sipalne komponente (fotonski pritisk) v smeri širjenja žarka in gradientne komponente v smeri največjega gradienta intenzitete žarka. Če je gradientna komponenta večja od sipalne komponente, je delec ujet v točki, v kateri se uravnotežijo sila teže, vzgon in optična sila.

Optična pinceta je sestavljena iz treh glavnih elementov: laserja, sistema za krmiljenje laserskega snopa in objektiva z veliko numerično aperturo. Pinceta je običajno postavljena na invertni optični mikroskop, saj v tem primeru gravitacijska sila na delec avtomatsko nasprotuje sipalni komponenti optične sile, kar omogoča stabilnejše ujetje delca v prostoru. Obstaja več načinov krmiljenja laserskega snopa: z zrcali na piezo elementih, s prostorskim modulatorjem svetlobe (holografska optična pinceta) ali z akusto-optičnimi deflektorji.

V raziskavah smo uporabljali optično pinceto (LTM-N2000-A, Aresis), zgrajeno okrog invertnega optičnega mikroskopa (Nikon Eclipse TE2000-U) z motorizirano mizico (Prior OptiScan II) in vodno imerzijskim objektivom (Nikon NIR Apo 60x/1.0w) ter Ar⁺ ionskega kontinuiranega laserja (Coherent, Innova 90C-4, valovna dolžina 514.5 nm in maksimalna moč 1.7 W). Laserski snop usmerjata dva pravokotno postavljena akusto-optična deflektorja (AA Opto-electronic, DTSXY-400-532, akustična frekvenca 115 – 160 MHz), akustično valovanje zanju pa proizvaja računalniško nadzorovan kontroler za krmiljenje laserskega snopa (Aresis, BSC-01). Ta omogoča nanometrsko natančnost določanja lege pasti in časovno deljenje snopa na več tisoč hkratnih neodvisnih optičnih pasti. Običajna delovna moč optične pasti v ravnini vzorca je ustrezala 30 – 70 mW. Sliko vzorca zajema monokromatska CMOS kamera (PixeLINK, PL-A741, 1280x960 pikselov, fizična velikost piksla 6.7 μm), ki podpira snemanje s hitrostjo do 1000 slik na sekundo. Analizo video posnetkov smo opravili s programom *PartTrack* [144], ki omogoča sledenje delcev z nanometrsko natančnostjo. Shema postavitve optične pincete je prikazana na sliki 6.

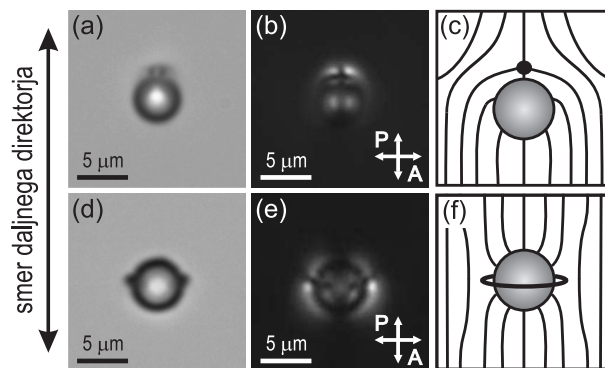


Slika 6: Shema postavitve optične pincete. Laserski snop je razširjen in voden skozi par pravokotno postavljenih akusto-optičnih deflektorjev na vhodno zenico objektiva z veliko numerično aperturo. Glavni računalnik nadzira krmilnik laserskega snopa, kamero in motorizirano mizico na invertnem mikroskopu.

Urejanje koloidov v ograjenih nematskih plasteh

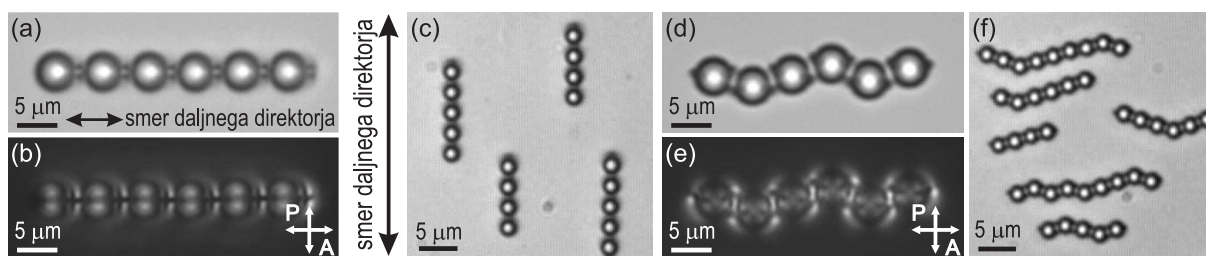
Elastični dipoli in kvadrupoli

Posamezni mikrometrski delci sferične oblike s homeotropnimi površinami tvorijo v ograjenem nematskem tekočem kristalu elastične dipole in kvadrupole (slika 7). Elastični dipoli in kvadrupoli so med seboj energijsko (meta)stabilni, pri čemer razliko energij določajo fizikalni parametri: velikost delcev, jakost sidranja na površinah, ograjenost in zunanje polje. Hiperbolični -1 točkovni defekt se pri elastičnem dipolu običajno odpre v majhen obroček [222,140,141]. Lega obročka, ki smo jo določili z analizo mikroskopskih posnetkov, je na razdalji $1.36r$ od središča koloidnega delca (r je njegov polmer), kar kvalitativno ustreza vrednostim v literaturi [131]. Pri elastičnem kvadrupolu radij defektnega Saturnovega obroča ustreza $1.28r$.



Slika 7: Homeotropna sferična delca v nematskem tekočem kristalu. (a) Elastični dipol s prepoznavnim hiperboličnim defektom (črna točka ob površini delca) v depolarizirani svetlobi in (b) med prekrizanimi polarizatorjema. (c) Shematska predstavitev direktorskega polja ima simetrijo električnega dipola. (d) Elastični kvadrupol z defektnim obročem v depolarizirani svetlobi in (e) med prekrizanimi polarizatorjema. (f) Direktorsko polje ima v tem primeru kvadrupolno simetrijo.

Strukturni prehod med elastičnim dipolom in kvadrupolom lahko sprožimo pri ustrezni debelini nematskih plasti z nenadnim faznim preходом iz izotropne v nematsko fazo v neposredni okolici koloida. Ta dogodek je stohastične narave, zato je (meta)stabilnost dipolne oziroma kvadrupolne konfiguracije odvisna od trenutnega poteka faznega prehoda in upravljanja optične pasti.



Slika 8: (a) Koloidna veriga, sestavljena iz elastičnih dipolov v planarni nematski plasti, fotografirana v depolarizirani in (b) polarizirani svetlobi. (c) Linearne dipolne verige se ob primerni koncentraciji delcev spontano sestavijo. (d-f) Elastični kvadrupoli v uniformnem nematskem polju spontano tvorijo linearne in nazobčane verige zaradi dveh ekvivalentnih bočnih stabilnih leg. Povzeto po referencah [80,81].

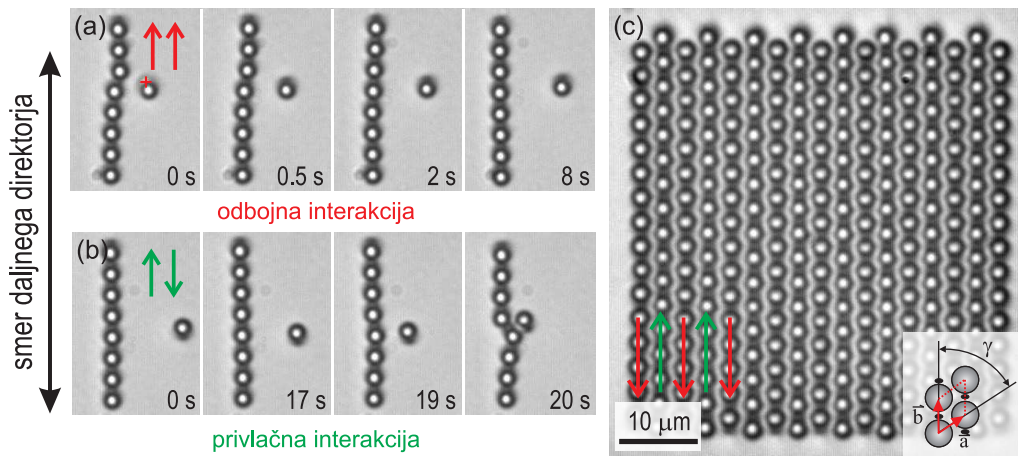
Interakcije med elastičnimi dipoli in kvadrupoli so močno anizotropne in v limiti daljnega polja sledijo prostorski odvisnosti iz enačb (6.18)-(6.20). Par elastičnih dipolov ima v uniformnem polju dve stabilni konfiguraciji. Antiparalelna dipola se privlačita bočno, paralelna dipola pa tvorita linearno verigo v smeri daljnega direktorja (slika 8). Kvadrupolni par ima dve simetrični bočno stabilni legi, kjer zveznica med delcema opiše kot $\sim 73^\circ$ z direktorjem na veliki oddaljenosti od delcev. Pari kvadrupolnih delcev se ob primerni koncentraciji sestavijo v linearne in nazobčane

kvadrupolne verige (slika 8). Tipični velikostni red meddelčnega potenciala za dva elastična dipola je nekaj $1000 k_B T$, za dva kvadrupola pa nekaj $100 k_B T$.

Dvodimenzionalni dipolni in kvadrupolni nematski koloidni kristali

Elastične dipole in kvadrupole lahko kontrolirano sestavimo v 2D nematske koloidne kristale z optično pinceto. Za vezavo delcev v periodično kristalno strukturo so odgovorne meddelčne strukturne sile. Stabilnost 2D nematskih koloidnih kristalov lahko kvalitativno razložimo v okviru dveh nasprotujočih si mehanizmov. Po eni strani poskuša tekoči kristal ohraniti čim manjši del prostora, v katerem je orientacija molekul elastično deformirana, kar učinkovito stiska kristalno ureditev delcev. Po drugi strani pa tekoči kristal poskuša v tem istem ograjenem prostoru zmanjšati elastično deformacijo ureditve molekul, ki posledično razpenja ureditev delcev. Občutljivo ravnovesje med tema dvema mehanizmoma tako določi natančen pozicijski in orientacijski red v nematskem koloidnem kristalu.

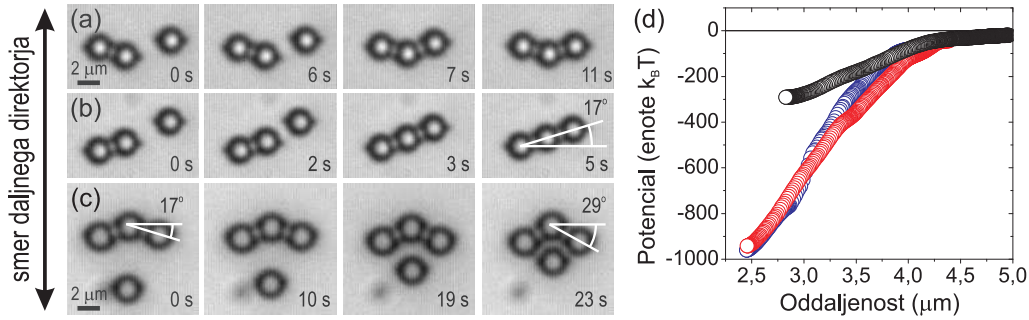
Slika 9 prikazuje princip in končni rezultat sestavljanja 2D dipolnega nematskega koloidnega kristala iz 280 steklenih kroglic s premerom $2.32 \mu\text{m}$. Direktorsko polje ima lokalno dipolno simetrijo, ki preko hiperboličnih točkovnih defektov stabilizira antiparalelno ureditev dipolnih verig. Eksperimentalne vrednosti mrežnih konstant osnovne celice dipolnega kristala so: $a = 2.95 \mu\text{m}$, $b = 2.84 \mu\text{m}$ in $\gamma = 61^\circ$. Postopek sestavljanja takšnega koloidnega kristala z optično pinceto je relativno preprost in dolgotrajen, saj lahko zgolj z natančno manipulacijo posameznih koloidnih delcev postopoma zgradimo pravilno periodično strukturo. Pri tem je pomembno kontroliranje lege hiperboličnih točkovnih defektov in posledično izbiranje orientacije elastičnih dipolov. To enostavno dosežemo z optično pastjo, ki lokalno stali nematsko tekočokristalno fazo in ujame izbrani koloidni delec. S premikom optične pasti v željeno smer (gor ali dol) in z nenadnim lokalnim faznim preходом po ugašanju pasti določimo lego pripadajočega defekta glede na delec (zgoraj ali spodaj). Na ta način postopoma sestavimo linearne dipolne verige, ki se v primeru antiparalelne orientacije bočno privlačijo in tvorijo stabilno periodično strukturo. Vezavna energija vzdolž dipolnih verig znaša $\sim 5000 k_B T$, prečno na verige pa $\sim 3500 k_B T$ v primeru $2.32 \mu\text{m}$ velikih delcev. Takšna kristalna struktura je izredno robustna, odporna na manjše mehanske obremenitve in se lahko v laboratorijskih pogojih ohrani več mesecev.



Slika 9: (a) Vzpostavna orientacija dveh sosednjih elastičnih dipolov povzroči odbojno interakcijo med njima. (b) Če je smer dipolnih defektov nasprotna, dosežemo izrazit privlak izoliranega delca na koloidno verigo. (c) 2D dipolni nematski koloidni kristal v katerem hiperbolični točkovni defekti stabilizirajo urejeno strukturo. Kristal je sestavljen iz 280 steklenih kroglic, ki so razporejene v antiparalelne dipolne verige. Parametri osnovne celice ustrezajo $a = 2.95 \mu\text{m}$, $b = 2.84 \mu\text{m}$ in $\gamma = 61^\circ$. Povzeto po referenci [80].

Spontano urejanje elastičnih kvadrupolov pri veliki koncentraciji delcev vodi do nastanka heksagonalnih skupkov. Kontrolirano sestavljanje kvadrupolnih skupkov z optično pinceto razkrije

anizotropne interakcije med posameznimi delci (slika 10). Privlak vzdolž kvadrupolne verige je namreč trikrat močnejši od privlaka v prečni smeri. Kljub temu ima osnovna celica kvadrupolnega skupka obliko romba in jo lahko periodično dodajamo v dveh pravokotnih smereh. Tako nastali 2D kvadrupolni koloidni kristal je šibkeje vezan kot dipolni, kar se opazi v precejšnji občutljivosti na zunanje motnje. V ravnovesju so mrežne konstante osnovne celice kvadrupolnega koloidnega kristala, sestavljenega iz $2.32 \mu\text{m}$ velikih kroglic, enake $a = 2.69 \mu\text{m}$, $b = 3.01 \mu\text{m}$ in $\gamma = 56^\circ$. Zaradi anizotropnega privlaka med koloidnimi delci, ki je posledica nematske elastičnosti, se tak kristal sčasoma razgradi na posamezne skupke kvadrupolnih verig [81].



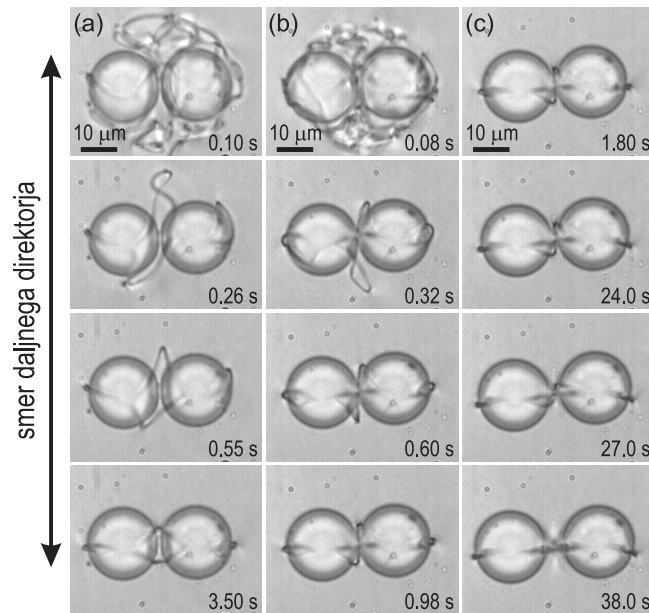
Slika 10: Posamezne kvadrupolne delce sestavimo v (a) nazobčane oziroma (b) ravne kvadrupolne verige z optično pinceto. (c) Opazimo tudi lateralni privlak med izoliranim koloidnim delcem in kvadrupolno verigo, ki vodi do nastanka 2D koloidnega četverčka. Tak četverček v obliki romba je osnovna enota periodično grajene heksagonalno mreže kvadrupolnega koloidnega kristala. (d) Meddelčna interakcija je anizotropna in znaša nekaj $100 k_B T$. Povzeto po referenci [81].

Množično manipulacijo koloidnih delcev v tankih nematskih plasteh lahko dosežemo z uporabo izmeničnega električnega polja. S kombinacijo elektrod in vmesnih neprevodnih pasov na substratu tekočerkristalne celice pripravimo območja z in brez možnosti vklopa prečnega električnega polja. Koloidni delci se pod vplivom električnega polja z jakostjo nekaj $\text{V}/\mu\text{m}$ in frekvenco nekaj 10 Hz zaradi negativne dielektroforeze (dielektričnost delcev je manjša od dielektričnosti tekočerkristalnega medija) enakomerno gibljejo v nasprotni smeri drgnjenja in napolnijo prostor med elektrodama. Pri nizki koncentraciji delcev le-ti po prehodu meje med elektrodo in neprevodnim pasom spontano tvorijo dipolne verige, ki se zaustavijo in nakopičijo na robu neprevodnega območja. Povečana koncentracija delcev vpliva na razporeditev in defektno konfiguracijo posameznih koloidov. Sčasoma se večina točkovnih defektov zaradi ograjenosti odpre v Saturnove obroče, ki se nato še dodatno upognejo in tako zmanjšajo elastično deformacijo tekočega kristala med tesno zloženimi delci. Kombinacija opisanih dejavnikov privede do nastanka 2D heksagonalnih koloidnih struktur z ravnim oziroma nazobčanim robom na območju med elektrodama. Stabilnost teh kristalitev je zagotovljena zgolj v času vklopljenega električnega polja, kasneje pa struktura zaradi obilice nepravilnosti v kristalni mreži in šibke vezavne energije postopoma razpade na manjše skupke [96].

Zunanja parametra, ki ju največkrat uporabljamo za optimizacijo strukturnih lastnosti 2D nematskih koloidnih kristalov, sta debelina celice in temperatura. Debelina celice je globalni parameter, ki določa stopnjo ograjenosti sistema in vpliva predvsem na jakost in obliko meddelčnih potencialov. Površine celice, v kateri se nahaja tekoči kristal z dispergiranimi koloidnimi delci, namreč vplivajo na meddelčno interakcijo, saj omejujejo načine elastičnih deformacij medija in preko tega interagirajo z delci. Ko postane meddelčna razdalja primerljiva z debelino celice, močno sidranje tekočega kristala na njenih stenah relativno zmanjša vpliv enega koloida na direktorsko polje na mestu drugega koloida. Interakcija je zasenčena in pojema eksponentno s karakteristično dolžino, ki je sorazmerna z debelino celice [53]. Temperatura je v obravnavanih primerih predvsem lokalni parameter, ki deluje na fino strukturo možnih defektov, dokler ohranjamo sistem globoko v nematski fazi. Vpliv temperature na mrežne konstante koloidnih kristalov se lahko nekoliko ojača ob hkratni uporabi zunanega električnega polja.

Prepletene koloidne strukture v uniformnem nematskem polju

Tekoči kristal se v neposredni okolici koloidnih delcev pri enakih pogojih (ograjnost, zunanje polje, jakost sidranja) lahko uredi v različne strukture. Primer takšnega urejanja so dipolne in kvadrupolne koloidne strukture, ki soobstajajo v določenem območju. Absolutna stabilnost oziroma metastabilnost takih struktur je odvisna od njihove proste energije, pri čemer vsaki strukturi pripada lokalni minimum v prosti energiji. Energijska pregrada med različnimi strukturami je običajno mnogo večja od $k_B T$, zato so termične fluktuacije praviloma prešibke za sprožitev strukturnih prehodov. Stabilno konfiguracijo tekočega kristala okrog koloidnih delcev lahko dosežemo z nenadnim faznim prehodom iz neurejene izotropne faze v relaksirano nematsko fazo. Ob nenadnem padcu temperature se tvori množica defektov, ki v nekaj milisekundah razpadejo in se paroma izničijo. Natančna dinamika anihilacije defektov nas v tem primeru ne zanima, saj bomo nenadni prehod iz nematske v izotropno fazo (in obratno) uporabili za tvorbo kompleksnih metastabilnih konfiguracij defektnih linij. Nenaden dvig oziroma padec temperature v izbranem območju tekočokristalne plasti eksperimentalno dosežemo z optično pinceto, ki omogoča lokalizirano gretje vzorca. Laserski snop pincete najprej stali nematski red v izotropno fazo, nakar snop hipoma ugasnemo. Takoj zatem se začnejo tvoriti domene z naključno urejeno nematsko fazo. Sčasoma se velikost domen in stopnja nematskega reda v njih povečujeta, mejna neurejena območja med domenami pa se razvijejo v naključno postavljene in orientirane $+\frac{1}{2}$ in $-\frac{1}{2}$ defektne linije, ki se paroma izničujejo. V prazni nematski celici se skozi proces relaksacije izničijo vse defektne linije, saj ima uniformna ureditev nematika najnižjo prosto energijo in ničeln topološki naboj. V nematski celici s koloidnimi delci se doseganje ravnovesja bistveno spremeni, ker defektne linije ne morejo popolnoma izginiti zaradi kompenzacije topološkega naboja, ki ga ustvarijo delci [83].

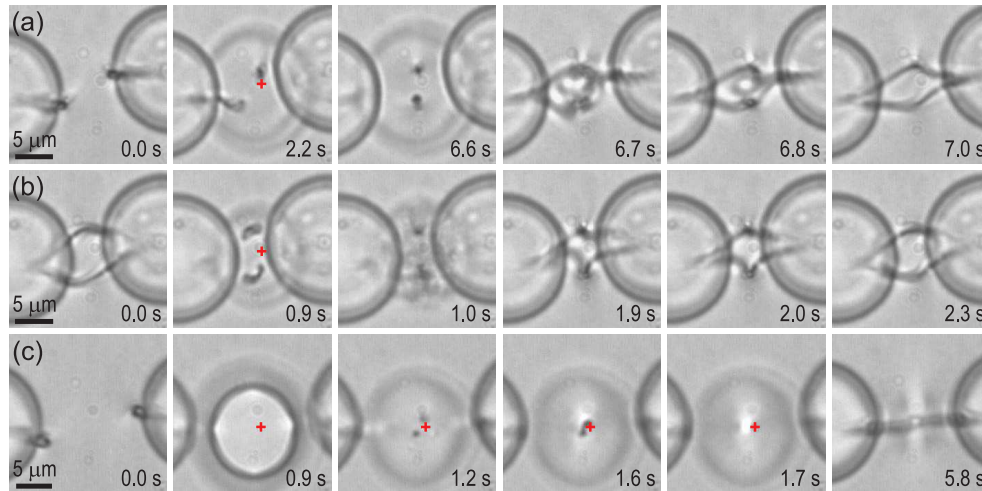


Slika 11: Prepletanje koloidnih parov z nenadnim upadom temperature po izklopu laserskega snopa. (a) Koloidni par z defektno strukturo osmice, ki jo razločno vidimo v depolarizirani svetlobi. (b) Proces nastajanja pletenice iz izotropne taline, ki se preko uravnovešanja defektnih linij stabilizira okrog koloidnih delcev. (c) Defektna struktura pletenice je metastabilna, zato se pretvori v prepleteni točkovni defekt [83].

Posebej zanimivo dogajanje lahko natančneje spremljamo na primeru dveh koloidnih delcev. Ob nenadnem faznem prehodu iz izotropne v nematsko tekočokristalno fazo opazimo pojav prepletenosti. Ker se defektne linije ne morejo popolnoma uravnovesiti, pride do nastanka metastabilnih konfiguracij, ki zajemajo več kompleksno prepletenih defektnih zank z ujetimi koloidnimi delci. Prepletanje koloidnih parov s tremi različnimi defektnimi strukturami je po-

drobno prikazano na mikroskopskih posnetkih (slika 11). Potek relaksacije je v vseh primerih podoben, vendar nikoli popolnoma enak zaradi stohastične narave posameznega faznega prehoda. Iz izotropne taline, ki zajame bližnjo okolico koloidnih delcev, se najprej tvori množica defektov, ki se uravnovešajo v končno metastabilno stanje. Po relaksaciji ostane zgolj ena sama $-\frac{1}{2}$ defektna linija, ki obkroža oba delca in tvori nov topološko stabilen objekt. V prvem primeru dobimo defektno strukturo *osmice* [slika 11(a)], poleg tega pa odkrijemo še defektni strukturi *pletence* [slika 11(b)] in *prepletenega točkovnega defekta* [slika 11(c)]. Vsi trije prepleteni pari so bili numerično napovedani in potrjeni v okviru fenomenološkega Landau-de Gennesovega modela proste energije [8]. Numerični eksperiment je presenetljivo natančno opisal realni fazni prehod in bistveno prispeval k pravilni razlagi kompleksnih konfiguracij prepletenih parov [83,222].

Prepletanje koloidnih delcev z nenadnim upadom temperature je stohastičen proces, kjer posamezna prepletena struktura nastane z določeno verjetnostjo. Če izvedemo množico zaporednih nenadnih dvigov in padcev temperature, pride v približno polovici primerov do prepletenja, medtem ko se v drugi polovici primerov tvorita dva ločena Saturnova obroča. Vse prepletene strukture so metastabilne v primerjavi s strukturo dveh Saturnovih obročev, saj imajo za 0.3 % (osmica), 0.9 % (pletencia) in 0.7 % (prepleteni točkovni defekt) višjo celotno prosto energijo [83]. Osmica in pletenica sta obenem kiralna topološka objekta, saj lahko zlomita zrcalno simetrijo. Strukturi z levo in desno ročnostjo sta enako verjetni in imata enako prosto energijo. Odkritje spontane tvorbe kiralnih objektov v nekiralnem mediju je posebej zanimivo za uporabo v optiki.



Slika 12: Pojav prepletenih koloidnih struktur lahko natančneje nadziramo z omejenim obsegom nenadnega faznega prehoda. (a) Osmica nastane, ko dva koščka Saturnovih obročev z optično pastjo zvijemo v klobčič, ki se po izklopu pasti razpleta v prepleteno strukturo. (b) Postopek je reverzibilen in izveden pod temperaturo faznega prehoda. (c) Prepleteni točkovni defekt pa nastane le ob taljenju nematske faze.

Trije prepleteni koloidni pari so si v osnovi precej podobni, saj v vseh primerih sklenjena defektna zanka obkroži oba delca. Tak način vezave je zelo robusten in stabilen, kar potrjuje izmerjeni vezavni potencial ob raztegovanju zanke v smeri zveznice para [83]. Ta je za vse tri strukture približno enak in znaša $\approx 10000 k_B T$ v primeru $5 \mu\text{m}$ velikih delcev [83]. Vezavna energija v omenjeni smeri je torej za red velikosti močnejša kot pri neprepletenih strukturah elastičnih dipolov in kvadrupolov. Zanimivo je, da je vezavni potencial za vse prepletene strukture strunast. Tako prostorsko odvisnost lahko kvalitativno razložimo z linearnim podaljševanjem defektnih linij ob raztezanju koloidnih struktur, vendar pri tem zanemarimo učinek elastičnega gubanja, zvijanja in upogibanja na manjši skali.

Prepletene strukture topološko določa njihov topološki naboj q . K celotnemu topološkemu naboju prispevajo delci, ki efektivno nosijo posamezen naboj $+1$ in defektne zanke, ki naboj delcev ustrezno kompenzirajo. Prepletene strukture tvorimo v geometriji uniformnega nematskega polja, ki zahteva, da je celoten topološki naboj prepletene strukture enak 0. Iz te omejitve

izrazimo topološki naboj prepletene defektne linije. Ta je po velikosti enak številu delcev, ki jih ta linija prepleta. Prepleteni pari osmice, pletenice in prepletenega točkovnega defekta imajo topološki naboj -2 , saj velja: $-2 = -(1 + 1)$.

Prepletenost lahko posplošimo iz koloidnih parov na koloidne verige. Razširjene defektne strukture na osnovi osmic in prepletenega točkovnega defekta stabilizirajo linearne verige. Pri verigi osmic ena sama defektna zanka preplete vse delce. Takšna veriga je kiralen objekt, v katerem se levo oziroma desnoročni deli lahko izmenjujejo [222]. Verigo iz prepletenih točkovnih defektov povezuje en sam defektni obroč, ki obkroži vse delce, med njimi pa so umeščeni posamezni -1 hiperbolični točkovni defekti. Postopek prepletanja koloidnih delcev v splošnem ni omejen zgolj na enodimenzionalne (1D) objekte, ampak ga lahko nadgradimo tudi v 2D in 3D prepletene strukture, znane pod imenom *nematske pletenine* [85]. Mehanizem je enak kot pri koloidnih parih, kjer z nenadnim faznim prehodom iz izotropne v nematsko fazo tvorimo množico defektov, ki imajo v tem primeru ogromno možnih konformacij, od katerih je večina nestabilnih in hitro razpadejo skozi zaporedje vmesnih stanj v končno prepleteno ali neprepleteno ravnovesno stanje. Teoretični izračuni kažejo možnost obstoja 2D prepletenih koloidnih kristalov v uniformnem nematskem polju, vendar je periodičnost konformacij močno odvisna od števila delcev v osnovni celici [85]. Večje število delcev izrazito poveča število možnosti in omogoči tvorbo še bolj zapletenih defektnih vzorcev, majhne razlike v prosti energiji pa so glavni razlog, da se defektni vzorci hitro pretvorijo v novo konformacijo že ob najmanjši zunanji motnji. V eksperimentih nam zaradi pravkar navedenih razlogov 2D prepletenih struktur kljub večkratnim poskusom ni uspelo uresničiti. Ugotovili smo, da je prostorsko manipulacijo defektnih linij veliko enostavneje nadzirati v kiralnem nematskem polju, ki odpravi simetrijske omejitve planarne geometrije.

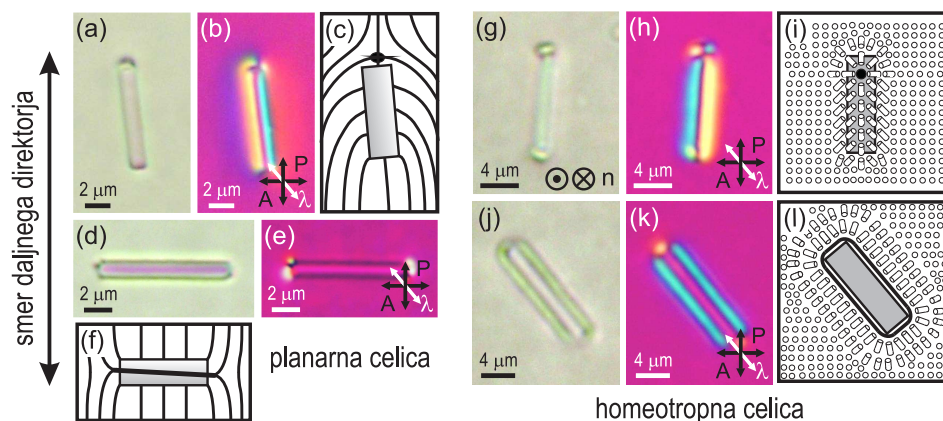
Interakcije mikropalčk v uniformnem nematskem polju

Koloidni delci nesferičnih oblik so posebej zanimivi, ker lahko zlomijo zrcalno simetrijo direktorskega polja, kar povzroči silo in navor na ravnovesno orientacijo delcev v nematskem mediju. Doslej je bilo objavljenih nekaj teoretičnih študij o ravnovesnih orientacijah, pripadajočih defektnih strukturah in parskih interakcijah paličastih delcev v nematskem tekočem kristalu [247–254]. Večina raziskav je bila opravljena na nanometrski velikostni skali v okviru molekularne dinamike, vendar te študije niso bile eksperimentalno preverjene zaradi pomanjkanja ustreznih materialov in kemijskih postopkov za pripravo homogenih koloidnih disperzij. Kljub temu lahko na podlagi simetrije in osnovnih lastnosti meddelčnih potencialov paličastih koloidov v nematiku uganemo ključne konfiguracije direktorskega polja, saj le-te niso odvisne od velikosti delcev, temveč zgolj od sidranja tekočerkristalnih molekul na ograjujočih površinah [21,129].

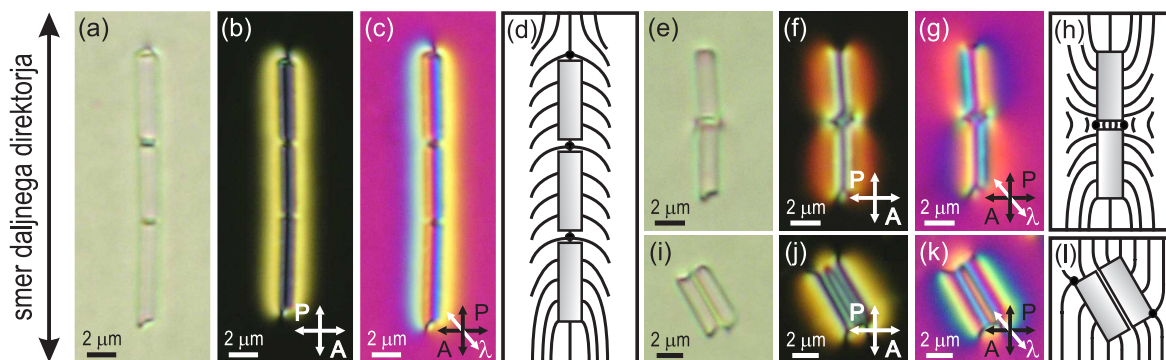
V naših eksperimentih smo se osredotočili na analizo defektnih struktur v neposredni bližini paličastih delcev mikrometrskih dimenzij, ki smo jih ogradili z uniformnim nematskim poljem. Pripravili smo disperzijo steklenih mikropalčk s premerom $1.5\ \mu\text{m}$ in povprečno dolžino $8\ \mu\text{m}$ v nematskem tekočem kristalu 5CB. Površina mikropalčk je bila obdana s tanko plastjo surfaktanta DMOAP, ki zagotavlja močno homeotropno sidranje tekočerkristalnih molekul. Analiza orientacij večjega števila mikropalčk v tanki planarni celici in uporaba polarizacijske optične mikroskopije sta potrdili obstoj dveh pričakovanih defektnih struktur: dipolne in kvadrupolne. Dipolne mikropalčke se z dolgo osjo poravnajo v smeri daljnega direktorja, pri čemer se točkovni defekt nahaja pri vrhu delca [slika 13(a-c)]. Direktorsko polje v neposredni okolici dipolne mikropalčke močno spominja na direktorsko polje v bližini dipolne verige, sestavljene iz koloidnih kroglic podobne velikosti. Kvadrupolne mikropalčke se spontano orientirajo pravokotno na smer daljnega direktorja, pri čemer Saturnov obroč objame delec vzdolž njegove dolge osi [slika 13(d-e)]. Zaradi močne ograjenosti nematskih plasti in nesferične oblike delca spremlja preobrazbo točkovnega defekta v defektno linijo tudi sprememba orientacije mikropalčke, ki tako preko sproščenega navora zmanjša elastično deformacijo okoliškega tekočega kristala [253,254]. Proces reorientacije delcev in morebitne spremembe defektnih struktur lahko natančneje raziščemo z

uporabo optične pincete. Topološki defekt enostavno manipuliramo z laserskim snopom in s tem določamo različne metastabilne orientacije vzdolž koloidnega delca [35]. Pri daljših mikropalčkah opazimo stabilno lego Saturnovega obroča tudi v ravnini krajše osi delca, kar ustreza prisilnemu odprtju točkovnega defekta. Rezultati teh raziskav kažejo, da so ravnovesne defektne strukture v okolici palčk topološko enake defektnim strukturam v okolici kroglic. Ta ugotovitev ni presenetljiva, če upoštevamo dejstvo, da na nastanek določene defektne strukture vplivajo predvsem robni pogoji na ograjujočih površinah, jakost sidranja in profil daljnega direktorskega polja.

Obe defektni konfiguraciji lahko opazujemo tudi v geometriji homeotropne celice. Točkovni defekt se v primeru dipolne mikropalčke preseli na spodnjo oziroma zgornjo površino delca [slika 13(g-i)], medtem ko Saturnov obroč mikropalčko obkroži v ravnini slike [slika 13(j-l)]. Stabilnost posamezne defektne strukture je odvisna predvsem od razmerja med debelino celice in premerom mikropalčke ter jakosti sidranja tekočerkristalnih molekul na površini mikropalčk. Ravnovesna orientacija mikropalčke je v tem primeru poljubna, saj je direktor pravokoten na ravnino njenih osi.



Slika 13: (a-c) Dipolna mikropalčka se v planarni nematski celici poravna vzdolž daljnega direktorja in spominja na dipolno verigo iz kroglic. (d-f) Kvadrupolna mikropalčka v tanjših nematskih plasteh se spontano orientira pravokotno na smer daljnega direktorja. Saturnov obroč jo obkroža vzdolž dolge osi. (g-i) Dipolna mikropalčka v homeotropni nematski celici s točkovnim defektom na zgornji površini. (j-l) Kvadrupolno mikropalčko v homeotropni celici prepoznamo po značilnem defektnem obroču, ki obkroža delec v ravnini slike. Različne barve, ki se pojavijo pri opazovanju vzorcev med prekržanimi polarizatorji z vstavljenim optičnim kompenzatorjem, predstavljajo dvolomnost tekočega kristala in pomenijo različno orientacijo tekočerkristalnih molekul ob površini delcev.



Slika 14: Ravnovesne konfiguracije dipolnih parov mikropalčk v planarni nematski celici. (a-d) Dipolna veriga iz mikropalčk. (e-h) Dve nasprotno orientirani mikropalčki se povežeta s pobeglim defektnim obročem ali pa tvorita rahlo zasukan antiparalelni dipolni par (i-l). Shematske ilustracije prikazujejo ureditev direktorskega polja v okolici delcev in so izdelane na podlagi informacij, ki jih posredujejo polarizacijski posnetki vzorcev. Te strukture so se samosestavile med polnjenjem tekočerkristalne celice.

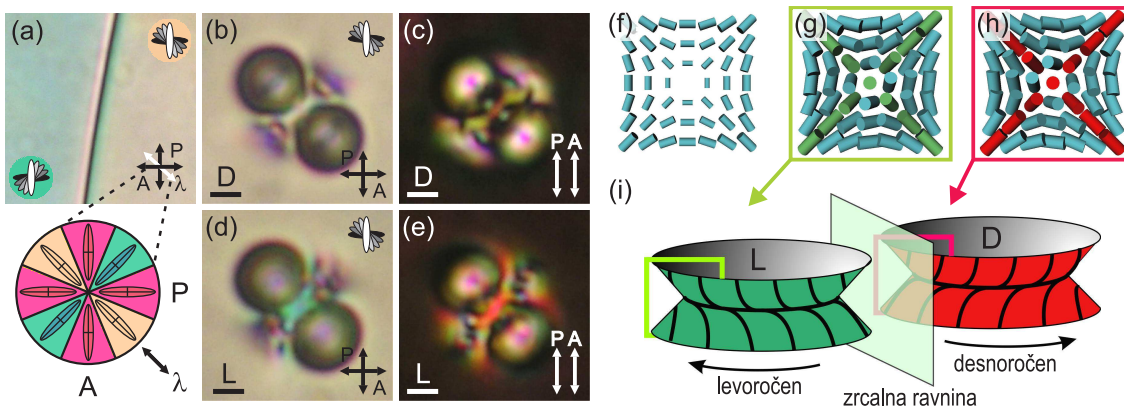
Parske interakcije dipolnih in kvadrupolnih mikropalčk so v osnovi zelo podobne interakcijam sferičnih koloidov primerljivih velikosti. Vzporedna orientacija dipolnih mikropalčk povzroči odbojno interakcijo, medtem ko antiparalelna postavitev sproži močan privlak na razdalji nekaj μm . Meddelčni potenciali dosegajo vrednosti nekaj $1000 k_B T$ in so neposredno primerljivi s privlakom med dvema dipolnima verigama iz koloidnih kroglic [35]. Kvadrupolne mikropalčke se uredijo v pare in bočno zložene skupke, ki obetajo gradnjo periodičnih struktur v dveh ali več nivojih. Ključni parametri za doseg tega cilja so enotna dolžina in ustrezen premer mikropalčk v mikrometrskem območju ter nadzor koncentracije delcev v omejeni geometriji tekočerkristalne celice. Žal so ti parametri v praksi težko dosegljivi, posebej v primeru steklenih delcev. Nekoliko več možnosti za uspeh lahko ponudijo sodobne litografske tehnike, ki omogočajo izdelavo koloidnih delcev poljubnih oblik in s tem tudi študij meddelčnih interakcij v anizotropnih topilih. Nedavne raziskave v tej smeri namreč že ponujajo prve rezultate [36,259].

Pobegle defektne strukture v kiralnem nematskem polju

Zvojna (twist) nematska celica s pravokotno postavljeno zgornjo in spodnjo planarno površino ustvari prostorsko odvisno direktorsko polje, ki energijsko stabilizira pobegle defektne strukture. Ustvarijo se levo in desnorsučne domene, odvisno od smeri zasuka tekočerkristalnih molekul. Nastale koloidne strukture v dani zvojni domeni so enakovredne strukturam v nasprotno sučni domeni, če uporabimo simetrijsko operacijo zrcaljenja. Zanimivo je, da točkovni defekti v kiralnem nematskem polju na kratkih medsebojnih razdaljah postanejo metastabilni, zato se običajno pretvorijo v pobegle hiperbolične defektne obroče z nižjo vezavno energijo.

Pari delcev s pobeglimi hiperboličnimi defektnimi obročji

Geometrija celice z zvitim direktorjem stabilizira koloidne strukture s pobeglimi hiperboličnimi defektnimi obročji, znane pod imenom 'bubble-gumi' [131,136,233]. Te strukture so bile doslej redko proučevane, saj jih zaradi specifične in energijsko potratne konfiguracije le redko opazimo v planarnih tekočerkristalnih celicah. V teh strukturah nesingularno direktorsko polje poveže delce v topološko neločljive pare, v katerih so delci podobno kot v prepletenih parih vezani z linearno odvisnim meddelčnim potencialom. Zvezno spreminjanje direktorja je možno zaradi pobega singularnih točkovnih defektov v nesingularne hiperbolične defektne obroče [136,233].



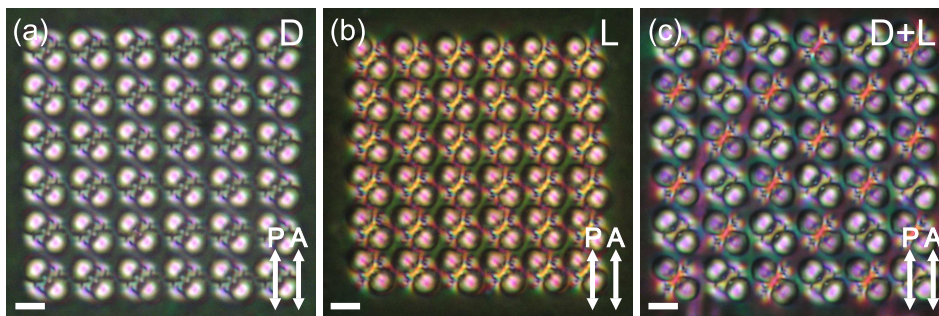
Slika 15: (a) Sučnost kiralne nematske domene določimo s pomočjo barve, ki se pojavi glede na smer zasuka med prekrizanimi polarizatorjema in vstavljeno λ ploščico. (b, c) Desnoročni in (d, e) levoročni par delcev, povezan z pobeglim hiperboličnim defektnim obročem med prekrizanimi oziroma vzporednima polarizatorjema v levosučni nematski domeni. (f) Prerez hiperbolične defektne linije, ki sočasno pobegne (g) gor in dol oziroma (h) dol in gor v dveh pravokotnih ravninah. (i) Ko pobeglo defektno linijo sklenemo, dobimo levoročni oziroma desnoročni pobegli defektni obroč. Singularnost v jedru defekta je na ta način odpravljena, kar močno zmanjša elastično deformacijo okoliškega nematskega polja.

Spontano samourejanje koloidnih parov s pobeglimi defektnimi obroči opazimo že med samim polnjenjem tekočerkristalne celice. Posamezni elastični dipoli so zasukani za 45° glede na smer drgnjenja na zgornji in spodnji površini celice in znotraj izbrane domene s točkovnimi defekti obrnjeni eden proti drugemu. Zaradi specifične geometrije celice pri interakciji dveh dipolov redko nastane antiparalelni par, ki je v kiralnem nematskem polju zgolj metastabilen, temveč se pogosteje tvori energijsko ugodnejši par delcev s pobeglim hiperboličnim defektnim obročem. Vezavno energijo takega para lahko ocenimo z uporabo optične pasti, s pomočjo katere razmaknemo vezana koloidna delca na določeno razdaljo, ugasnemo past in izmerimo hitrost njunega privlaka. Iz teh podatkov dobimo grobo oceno vezavne energije, ki znaša več kot $10000 k_B T$ v primeru $5 \mu\text{m}$ velikih delcev [97]. Kiralno nematsko polje torej dodatno stabilizira nesingularne topološke defekte na podoben način kot spinsko-orbitalna sklopitev elektronov v kiralnih magnetnih sistemih bistveno prispeva k nastanku skyrmionskih topoloških stanj [166,260,262].

Z optično manipulacijo pobeglega defektnega obroča lahko spremenimo orientacijo tekočerkristalnih molekul, ki tvorijo to defektno strukturo. Izkaže se, da lahko znotraj iste zvojne domene ustvarimo dve različni defektni strukturi, prikazani na sliki 15(b-e). Razlikujeta se po barvi nesingularnega defektnega obroča med prekrizanima oziroma vzporednima polarizatorjema, iz česar lahko sklepamo na različno smer pobega. To domnevo dejansko potrdimo s podrobnejšo analizo defektnih struktur v okviru Landau-de Gennesovega modela [8,222]. Za razliko od radialne defektne linije z ovojnim številom $+1$, ki lahko pobegne gor ali dol (linija poteka vzdolž osi z), imamo v tem primeru opravka s hiperbolično defektno linijo. Slednja ima ovojno število -1 in lahko hkrati pobegne gor in dol (oziroma dol in gor) v dveh pravokotnih ravninah [97]. Prerez hiperbolične defektne linije in njen pobeg v izbrano smer sta shematsko prikazana na sliki 15(f-i). Tak pobeg v tretjo dimenzijo močno zmanjša elastično deformacijo nematika, saj singularnost v jedru defekta izgine, vzpostavi pa se pobeglo direktorsko polje z le majhnimi variacijami stopnje nematskega reda. Ko pobeglo defektno linijo sklenemo v obroč, nastane kiralni topološki objekt v obliki rahlo zvitega toroida, ki je lahko levo ali desnoročen, odvisno od smeri pobega v izbranih ravninah. Pobegla defektna obroča sta deformirana podobno kot Saturnova obroča v kvadrupolnem paru, saj na ta način še dodatno zmanjšata elastično deformacijo zaradi zunanega zvoja. Pobegli hiperbolični defektni obroč je topološko homotopen (ekvivalenten) točkovnemu defektu s topološkim nabojem -2 . V zvojni celici imajo v dani zvojni domeni levo in desnoročni pobegli defektni obroči različne energije. V eksperimentih opazimo spontano tvorbo desnoročnih koloidnih parov v levosučni nematski domeni, medtem ko dobimo levoročne pare v isti domeni zgolj s pomočjo optične transformacije desnoročnega para. Numerični izračuni potrjujejo eksperimentalna opažanja in pokažejo, da ročnost pobeglega defektnega obroča pomembno vpliva na celotno energijo koloidnega para [222]. Ravnovesna vezavna energija desnoročnega para je namreč kar za 15 % nižja od vezavne energije levoročnega para v levosučni domeni [97].

Dvodimenzionalni koloidni kristali s poljubno ročnostjo defektnih obročev

Iz parov delcev s pobeglimi defektnimi obroči lahko z optično pinceto sestavimo množico novih 2D nematskih koloidnih kristalov s poljubno ročnostjo. Interakcija med pari delcev, ki jih postavimo na primerno medsebojno razdaljo, je privlačna neglede na začetni položaj parov in ni odvisna od ročnosti defektnih obročev. Izmerjen meddelčni potencial presega $5000 k_B T$ v primeru $5 \mu\text{m}$ velikih delcev [97]. Osnovna celica tako urejenih 2D nematskih koloidnih kristalov ima obliko kvadrata, ki izvira iz lokalne simetrije direktorskega polja v okolici defektnih obročev. Tak tip simetrije osnovne celice je v eksperimentih redko opažen, saj zahteva specifično štiristevno simetrijo vezave in ustrezen interakcijski potencial [264]. Tudi v tem primeru je kombinacija nasprotnega zasuka defektnih obročev in zunanega zvoja energijsko najugodnejša, kar omogoča kiralno segregacijo koloidnih struktur. Trije primeri 2D koloidnih kristalov s poljubno ročnostjo defektnih obročev so predstavljeni na sliki 16.



Slika 16: 2D nematski koloidni kristali, sestavljeni iz parov delcev s pobeglimi defektnimi obroči z uporabo optične pincete. (a) Mikroskopski posnetek desnoročne kristalne mreže v levosučni nematski domeni med vzporednima polarizatorjema. (b) Levoročni koloidni pari, sestavljeni v kvadratno kristalno mrežo znotraj levosučne nematske domene. (c) Koloidni kristal z mešano ročnostjo koloidnih parov v levosučni nematski domeni. Različne barve pomenijo različno orientacijo tekočerkristalnih molekul. Skala in velikost delcev ustrežata $5\ \mu\text{m}$.

Koloidi, vezani s pobeglimi in prepletenimi defektnimi strukturami, so si med seboj podobni. V obeh primerih defekti stabilizirajo topološko neločljive objekte, ki jih lahko razumemo kot nove osnovne elemente pri gradnji koloidnih struktur. Defektne zanke imajo v obeh primerih topološki naboj po velikosti večji od ena in v nematiku same brez stabilizacije z delci ne morejo obstajati. Prav tako oba tipa defektov povzročita in posredujeta strunast potencial med delci.

Vozli in zanke v kiralnem nematskem polju

Zadnji sklop raziskav smo posvetili 2D prepletanju defektnih zank v kiralnem nematskem polju. Nastale strukture so v topološkem smislu izredno bogate, saj zajemajo široko paleto vozlov, ki jih z optično pastjo spletemo okrog ustrezno razporejenih koloidov. Zaradi lažjega razumevanja teh pojavov se bomo najprej seznanili z osnovnimi pojmi matematične teorije vozlov.

Kratek uvod v teorijo vozlov

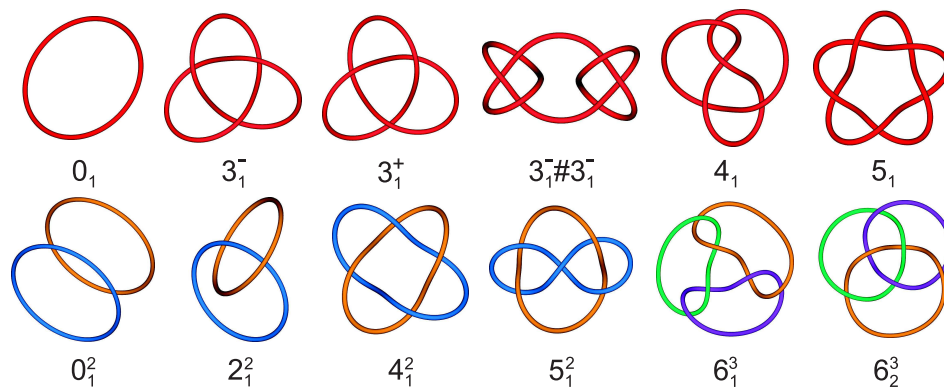
Vozli so povsod prisotni topološki objekti, simboli kompleksnosti, ki so navduševali ljudi od najzgodnejših začetkov človeške zgodovine. Ljudje že od nekdaj uporabljamo vrvi in s tem tudi različne tipe vozlov za različne namene. Nekateri od njih pridejo prav vsak dan, na primer pri zavezovanju čevljev ali kravate. Posebni vozli pa se uporabljajo pri jadranju, ribolovu, plezanju, pletenju kit in preprog ter nudenju prve pomoči [149]. Poleg tehnološke uporabnosti so vozli zanimivi tudi z estetskega in spiritualnega vidika, saj so v tem pogledu pogosto navdihovali srednjeveške umetnike pri ustvarjanju zapletenih keltskih vzorcev, izdelavi nakita in oblikovanju arhitekturnih dekoracij [151].

Začetki znanstvenega proučevanja vozlov in spletov segajo v sredino 19. stoletja, ko so se fiziki intenzivno ukvarjali z odkrivanjem zakonitosti atomov. Leta 1867 je William Thomson, pozneje znan kot lord Kelvin, predstavil vrtinčni model atoma, ki je domiselno razložil nekatere kvalitete kemijskih elementov [152]. Menil je, da je vesolje napolnjeno z nevidno tekočino, ki jo je imenoval eter, atomi v njem pa so vrtinci v obliki različnih vozlov. Ta teorija je navdušila škotskega fizika Petra Taita, ki je za proučevanje Kelvinovih idej izumil posebno napravo, s katero je lahko kontrolirano delal dimne obročke. S tem je nazorno pokazal: (i) da se vrtinci obnašajo kot neodvisni delci, (ii) da se pri trku odbijajo kot elastične trdnine, (iii) da imajo lastna nihanja okrog krožne oblike in (iv) da so neuničljivi. Predlagana teorija je zaradi svoje preprostosti in kot se je zdelo takrat, tudi smiselnosti, naredila velik vtis tudi na Jamesa Clerka Maxwella, ki je vozle iskal pri odkrivanju teoretičnih osnov elektromagnetnega polja [153]. Medtem se je Tait tako globoko poglobil v Kelvinovo teorijo snovi, da je sestavil neke vrste periodni sistem vrtinčne

snovi, v katerem so bili različni atomi predstavljeni z različno zavozlanimi vrtinci. Čeprav je bila Kelvinova teorija s prihodom kvantne mehanike dokončno ovržena, pa je Taitovo pionirsko delo sistemske ureditve vozlov postalo odlično izhodišče za razvoj matematične teorije vozlanja.

Danes je teorija vozlov zelo živahno raziskovalno področje, ki se samostojno razvija kot veja topologije in skuša odgovoriti na vprašanje ali je mogoče nek vozel preoblikovati v drugega in na podvprašanje, ali je mogoče izbrani vozel preoblikovati v trivialni vozel. Mnogo orodij iz teorije vozlov se uspešno uporablja tudi na področju statistične mehanike [156,157], fizike polimerov [154,155], biokemije [158] in v raziskavah topologije osnovnih gradnikov živih organizmov - molekul deoksiribonukleinske kisline (v nadaljevanju DNK) [160,161]. Matematični biologi so denimo v zadnjih desetletjih pravilno napovedali, da ima delovanje posameznih encimov na molekule DNK za posledico razvozlanje določenih segmentov, ki lahko sicer usodno vplivajo na prepis in podvajanje genskega zapisa med procesom celične delitve [162]. Matematična teorija vozlov med drugim omogoča identifikacijo teh vozlov in s tem pomaga odkrivati mehanizme delovanja nekaterih tipov virusov, kar bistveno pripomore k boju proti njim. V fiziki se v zadnjem času vozli pojavljajo predvsem v klasični teoriji polja [164], pri razumevanju turbulence v tekočinah, v teoretičnih raziskavah eksotičnih spinskih stanj in Bose-Einsteinovih kondenzatov [165–168] ter v optiki, kjer so nedavno s pomočjo holograma ustvarili osnovne vozle v optičnih vrtincih laserske svetlobe [172,173]. Kljub temu so eksperimentalne uresničitve vozlov v fiziki kondenzirane snovi relativno redke, saj smo še vedno na začetku njihovega odkrivanja, razumevanja in sestavljanja.

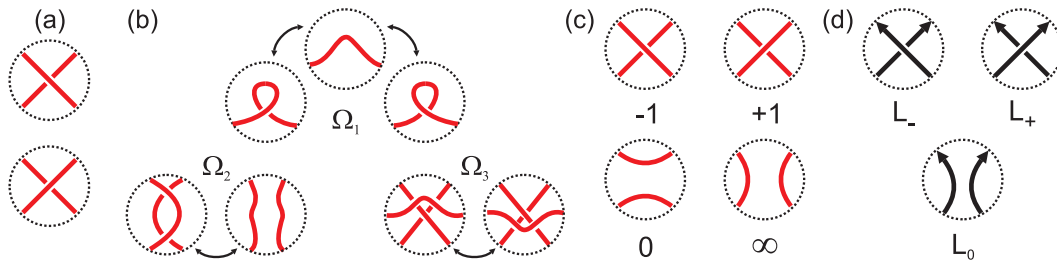
V okviru topologije je *vozel* definiran kot idealno elastičen objekt v obliki gladke sklenjene krivulje [151]. Vozli so objekti v trirazsežnem prostoru, na katerih lahko izvajamo neomejeno zaporedje različnih deformacij (upogibanje, raztezovanje, zvijanje), ki ne spreminjajo topologije objektov. Rezanje, trganje in lepljenje je strogo prepovedano. Najenostavnejši vozel je *trivialni vozel* ali *nevozel*, ki predstavlja navadno krožnico, par nespletenih krožnic pa imenujemo *ločen splet*. Najpreprostejši netrivialni vozel je *trilist*, preprosto spleteni krožnici, imenovani *Hopfov splet*, pa spadata v družino dvokomponentnih spleto. Nekaj primerov najbolj prepoznavnih vozlov in spleto je prikazanih na sliki 17.



Slika 17: Osnovni vozli in spleti, prikazani v obliki ravninskih diagramov: trivialni vozel 0_1 , levoročni trilist 3_1^- , desnorčni trilist 3_1^+ , ženski vozel $3_1^- \# 3_1^-$, osmica 4_1 , peterokraka zvezda 5_1 , ločen splet 0_1^2 , Hopfov splet 2_1^2 , Solomonov splet 4_1^2 , Whiteheadov splet 5_1^2 , zaprt splet treh krožnic 6_1^3 in Boromejski splet 6_2^3 . Zapisani simboli predstavljajo Rolfsenovo poimenovanje vozlov, kjer številka pove najmanjše število križišč izbranega vozla, indeks pa njegovo zaporedno številko med vozli z enakim številom križišč [151].

Dva vozla sta *ekvivalentna* oziroma istega *tipa*, če lahko enega preoblikujemo v drugega s topološko transformacijo, ki ne vsebuje rezanja. Vozle ponavadi rišemo s pomočjo projekcije na neko ravnino. Dobljeni sliki pravimo *diagram* oziroma *projekcija* vozla. V splošnem je lahko projekcija zelo komplicirana, zato se omejimo na projekcije, ki imajo končno mnogo *križišč*, pri čemer se nadvoz in podvoz sekata pod nekim kotom in nad njima ni še enega križišča [glej sliko 18(a)]. Kurt Reidemeister je leta 1927 dokazal, da lahko diagrama dveh ekvivalentnih

vozlov med seboj pretvorimo s končnim zaporedjem samo treh vrst premikov. Te premike, prikazane na sliki 18(b), imenujemo *Reidemeistrovi premiki*. Kot smo že nakazali, vsakega vozla ne moremo pretvoriti v drugega. Vozle tudi zato poimenujemo s številko in indeksom, v skladu s tradicionalnim Rolfsenovim načinom poimenovanja [174]. Številka predstavlja najmanjše število križišč, t.i. *križiščno število*, ki jih lahko ima voz, indeks pa pove, kateri po vrsti s takšnim križiščnim številom je ta voz (glej sliko 17). Konec 19. stoletja so že razlikovali veliko vozlov in sestavili tabele za tiste z manj kot deset križišči. V teh tabelah navajajo samo osnovne vozle, imenovane tudi *pravozli*, ki se jih ne da poenostaviti v dva preprostejša vozla. Poznamo tudi *sestavljene vozle*, ki nastanejo z lepljenjem osnovnih vozlov; primer ženskega vozla $3_1 \# 3_1^-$ je prikazan na sliki 17. Vsak voz lahko *orientiramo* tako, da izberemo smer obhoda, ki jo označimo s puščicami. Če na vozlu zamenjamo vlogi nadvoza in podvoza, dobimo *zrcalno sliko* prvotnega vozla. Taki vozli so *kiralni* in mednje spadata tudi levo oziroma desnoročni trilst. Obstajajo vozli, ki so zrcalni sami sebi. Tak primer je voz 4₁ s štirimi nadvozi, ki ga na kratko imenujemo osmica.



Slika 18: (a) Dovoljena tipa križišč, nadvoz in podvoz, ki ju uporabljamo v ravninskih projekcijah vozlov. (b) Reidemeistrovi premiki: Ω_1 - krivuljo zavijemo oziroma odvijemo, Ω_2 - del krivulje prestavimo čez drugo krivuljo, Ω_3 - krivuljo prestavimo čez križišče. (c) Osnovne Conwayeve determinante spleto s pomočjo katerih lahko zlepimo posamezne segmente vozlov. (d) Orientirane determinante za izračun zamenjalne identitete.

Osnovni cilj teorije vozlov je odkriti mnogo *invariant vozlov*, s pomočjo katerih lahko razlikujemo poljubne neekvivalentne vozle v poljubnih projekcijah. Med najbolj znane invariante prištevamo število komponent, križiščno število in *spletno število* [151]. Spletno število orientiranih spleto je definirano kot polovična vsota vseh križišč med dvema različnima komponentama spleta, pri čemer levoročna križišča prispevajo -1 , desnoročna pa $+1$. Uporabna geometrijska lastnost vozla je tudi njegova *zvitost*, ki je definirana podobno kot spletno število, le da tokrat seštejemo vrednosti vseh križišč. Zvitost vozla ni topološka invarianta, je pa uporabna pri določanju kiralnosti in izračunu drugih invariant.

Navedene invariante vozlov so žal precej šibke in nepopolne, zato jih ne moremo uporabiti za razlikovanje bolj zapletenih topoloških objektov z mnogo križišči. V ta namen so matematiki razvili nove postopke razločevanja neekvivalentnih vozlov, ki temeljijo na *polinomih vozlov*. Najpreprostejši med njimi so *Alexandrovi polinomi* $\Delta(t)$, ki jih je leta 1928 odkril James Alexander [151,176]. Alexandrov polinom dobimo naravnost iz projekcije vozla z lepljenjem posameznih segmentov; polinom trivialnega vozla je enak 1, polinom trilista pa ustreza $\Delta(t) = t - 1 + t^{-1}$. Kar zadeva odkrivanje novih računskih metod za prepoznavanje vozlov, ni bilo posebnega napredka vse do leta 1960, ko je John Horton Conway izumil nov, enostavnejši način konstrukcije Alexandrovih polinomov in vpeljal učinkovitejši način označevanja vozlov [177]. Njegova metoda temelji na *determinantah spleto*, prikazanih na sliki 18(c), ki predstavljajo nekakšne osnovne gradnike, iz katerih je mogoče zlepiti vse vozle z uporabo različnih algebraskih operacij. Najpogosteje se uporabi t.i. *zamenjalna identiteta*, sestavljena iz treh orientiranih determinant, ki se razlikujejo le na območju križišča. Zamenjalna identiteta Alexandrovega polinoma se glasi [151]:

$$\Delta(L_+) - \Delta(L_-) + \left(\sqrt{t} - \frac{1}{\sqrt{t}} \right) \Delta(L_0) = 0. \quad (6.24)$$

Pravi razcvet odkrivanja novih tipov polinomov spleto se je zgodil po odkritju *Jonesovega polinoma* $V(t)$ leta 1985 [179]. Vaughan Jones je za to odkritje pet let kasneje prejel tudi najvišje priznanje v matematiki, Fieldsovo medaljo. Definiramo ga s podobno zamenjalno identiteto kot Alexandrov polinom [178]:

$$\begin{aligned}\frac{1}{t}V_{L_+}(t) - tV_{L_-}(t) &= \left(\sqrt{t} - \frac{1}{\sqrt{t}}\right)V_{L_0}, \\ V_{\text{nevozel}}(t) &= 1.\end{aligned}\tag{6.25}$$

Čeprav se je Jonesov polinom izkazal za zelo močno invarianto, je njegova največja pomanjkljivost to, da ga s klasičnimi topološkimi sredstvi ne znamo preprosto opisati. Delno rešitev tega problema je predlagal Louis Kauffman z odkritjem preprostejše poti do izračuna Jonesovega polinoma. Njegova metoda temelji na *modelu stanj*, kjer s preprostim odstranjevanjem križišč v vozlu oziroma spletu generiramo množico nespletenih krožnic [156]. Vsako križišče razcepimo na vodoravno projekcijo A in navpično projekcijo A^{-1} , pri čemer vse kombinacije takšnih razcepov določajo stanje celotnega vozla. To stanje izračunamo preko *oklepajnega polinoma* kot vsoto vseh 2^n stanj vozla:

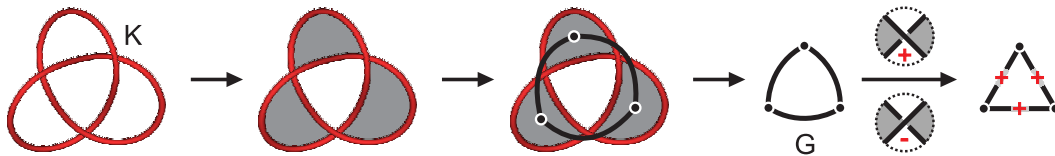
$$\langle K \rangle = \sum_{S_i} \langle S_i | K \rangle (-A^2 - A^{-2})^{|S_i|-1},\tag{6.26}$$

kjer $\langle S_i | K \rangle$ predstavlja produkt vseh A in A^{-1} na izbranem križišču in kjer $|S_i|$ ustreza številu nespletenih krožnic v posameznem stanju. Če obstaja n križišč, ki jih lahko razcepimo na dva načina, dobimo 2^n različnih stanj. Ker polinom iz enačbe (6.26) ni invarianten na prvi Reidemeistrov premik Ω_1 , moramo uporabiti še manjši trik, ki privede do konstrukcije *Kauffmanovega polinoma* $X(K)$, definirane z enačbo [156]:

$$X(K) = (-A)^{-3w(K)} \langle |K| \rangle,\tag{6.27}$$

pri čemer je $w(K)$ zvitost vozla in $\langle |K| \rangle$ oklepajni polinom neorientirane projekcije vozla. Kauffmanov trik se skriva v faktorju $(-A)^{-3w(K)}$, ki onemogoči moteči koeficient $A^{\pm 3}$ pri testiranju invariantnosti na prvi Reidemeistrov premik. Jonesov polinom $V(t)$ dobimo iz Kauffmanovega polinoma $X(K)$ zgolj z uporabo enostavne substitucije $A = t^{-\frac{1}{4}}$ [149,156].

Odkritje Jonesovih in Kauffmanovih polinomov ni sprožilo revolucije le v matematičnih krogih, temveč je bistveno poseglo tudi v osnove različnih vej fizike, še posebej v statistično mehaniko in kvantno teorijo grup [149]. Izkazalo se je namreč, da so statistični modeli, ki obravnavajo kolektivno obnašanje atomov oziroma spinov, posredno uporabni tudi za računanje novih invariant vozlov [156]. Osnova teh izračunov je določitev particijske funkcije, ki združuje informacije o medsebojnih interakcijah posameznih spinov [151]. Zanimivo je, da lahko particijsko funkcijo izračunamo s pomočjo konstrukcije grafov, ki predstavljajo pomembno skupino matematičnih objektov in so neposredno povezani s topologijo vozlov. Primer transformacije med trolistim vozлом in njegovim grafom je prikazan na sliki 19.

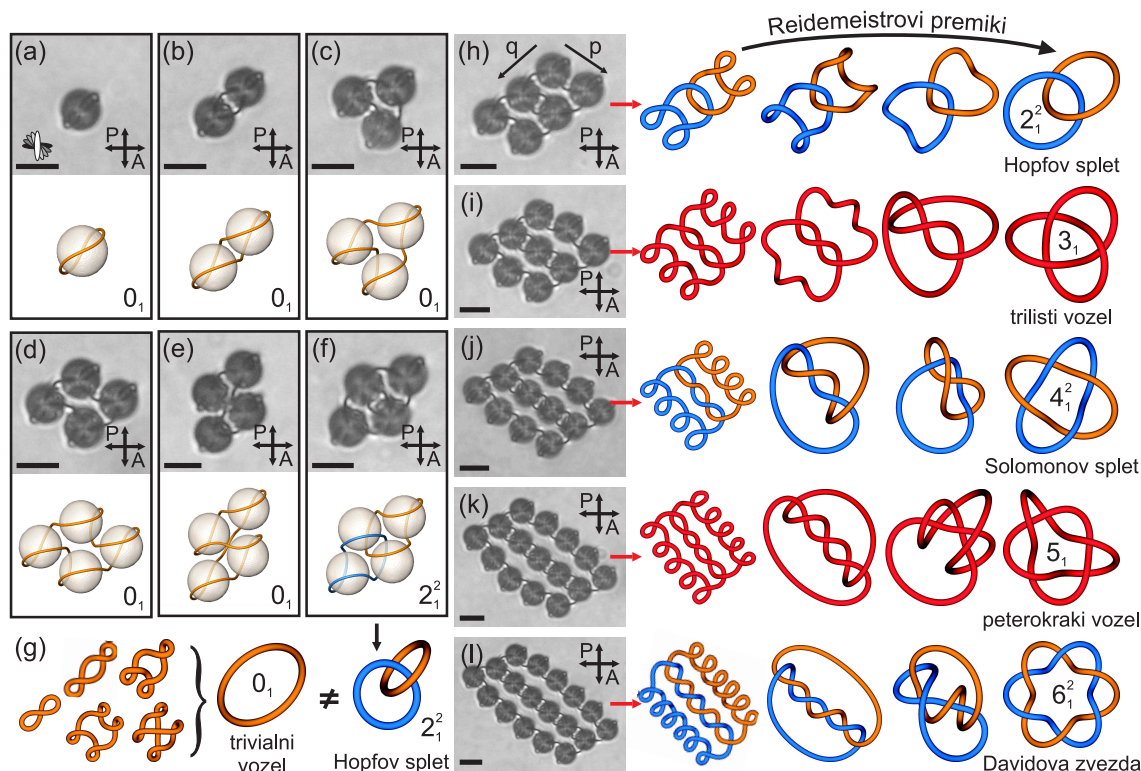


Slika 19: Prikaz enostavne transformacije projekcije vozla K v graf G . Notranja področja diagrama vozla najprej alternirajoče pobarvamo z dvema barvama, nato temnim področjem priredimo oglišča, ki jih na koncu med seboj povežemo preko vmesnih križišč. Glede na vrsto križišča lahko povezavi pripišemo tudi predznak, ki nam določi končno podobo grafa.

Mnogo dodatnih in podrobnejših informacij o teoriji vozlov lahko najdemo v vrsti specializiranih učbenikov [150,151,156,174,178,180] in v nekaj poljudno obarvanih prispevkih, namenjenih širšemu krogu bralcev [149,175,181].

Vozli in zanke iz prepletenih topoloških defektnih linij

Spontan pojav prepletenosti topoloških defektnih linij, ki obdajajo koloidne delce v tanki zvojni tekočokristalni celici, opazimo že med samim tokom koloidne disperzije. Posamezen koloidni delec povzroči kvadrupolno deformacijo bližnjega molekularnega polja, ki ga obda s Saturnovim obročem, le-ta pa se zaradi zmanjšanja vsiljene elastične deformacije zvije v obliki osmice. Zvojna domena, v kateri se nahajajo koloidni delci, obenem določi smer zasuka defektnih obročev, zato govorimo o kiralnih objektih, ki se morajo prilagoditi okoliškemu kiralnemu polju. Energijsko ugodno sklopitev dobimo v primeru, ko defektna zanka sledi zvoju okoliškega direktorja, zato v levosučni domeni opazimo zgolj delce z levoročnim defektnim obročem; glej sliko 20(a).



Slika 20: Zbirka prepletenih defektnih konfiguracij, ki ustrezajo nevozlu in topološkemu objektu iz družine torusnih vozlov in zank. (a) Saturnov obroč, zviti v obliki osmice, se spontano pojavi okrog homeotropnega sferičnega koloida. (b) Defektna struktura osmice preplete dva delca v obliki dvojne vijačnice. (c) Prepleten koloidni trojček predstavlja najpreprostejšo 2D prepleteno strukturo. (d) Dve prepleteni osmici se lateralno združita v zaokrožen četverček. (e) Osrednji del prekrizanega četverčka tvori struktura pletenice, ki razdeli osrednjo domeno na štiri enakovredne dele. (f) Splet dveh sklenjenih zank predstavlja prvi netrivialni topološki objekt z najmanjšim številom prepletenih delcev. (e) Enostavni zvoji ene zanke so ekvivalentni trivialnemu vozlu, ki je bistveno drugačen od Hopfovega spleta dveh zank. (h-l) Zaporedje osnovnih torusnih vozlov in zank dobimo na strukturno sorodnih $p \times 3$ koloidnih šablonah. Začetno defektno konfiguracijo preišemo v program za obdelavo vozlov [266] in jo preko zaporedja Reidemestrovih premikov relaksiramo v minimalno planarno projekcijo. Za klasifikacijo vozlov in zank uporabimo tradicionalno Rolfsenovo poimenovanje [174]. Vse eksperimentalne slike so posnete med prekrizanimi polarizatorjema in opremljene s 5 μm široko skalo.

Zaradi pravkar navedenih dejstev zviti profil direktorskega polja izdatno poveča stabilnost prepletenih koloidnih struktur, tako da ima par delcev, prepleten s strukturo osmice, najnižjo

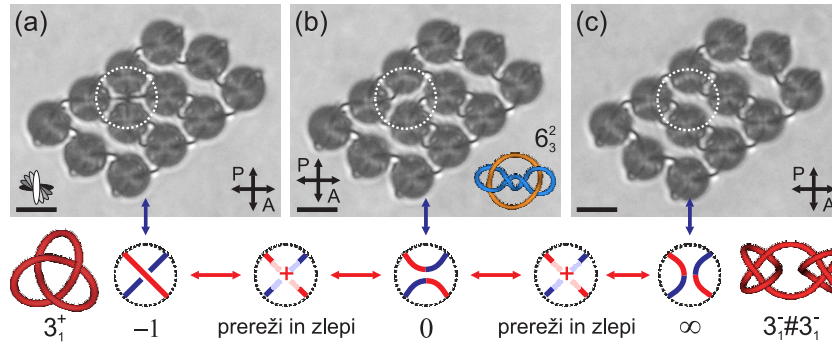
vezavno energijo; glej sliko 20(b). Zveznica takega prepletenega para se uredi pod kotom 45° glede na smer direktorja ob zgornji oziroma spodnji površini celice. Zato so defektne zanke najbolj razločno vidne v polarizirani svetlobi, kar nam omogoča relativno preprosto ugotavljanje prostorske razporeditve posameznih odsekov defektnih linij. Za nastanek prepletene verige osmic tako več ne potrebujemo nenadnega upada temperature iz izotropne v nematsko fazo, ampak za to zadošča že primerna razporeditev delcev v bližini ravnovesne lege. Pri nastanku osmic se namreč deformirajo le konci defektnih zank, medtem ko osrednji del direktorskega polja ostane praktično nespremenjen. Vezavna energija tako prepletenih delcev presega $10000 k_B T$, kar predstavlja eno najmočnejših sklopitvev v mehkih koloidnih sistemih nasploh.

Med tokom koloidne disperzije opazimo poleg prepletenih verig tudi preproste, spontano prepletene 2D skupke treh delcev, ki jih ni bilo mogoče stabilizirati v uniformnem nematskem polju. Primer takšnega prepletenega trojčka je prikazan na sliki 20(c). Spontano urejanje s tokom nadomestimo z mnogo natančnejšo optično manipulacijo posameznih defektnih zank. Uporabimo optično pinceto, ki nam omogoča enostavno izvajanje različnih operacij. Z optično pastjo zmerne moči (≈ 30 mW) premikamo delce v željeni smeri, močnejši laserski snop (≈ 60 mW) pa uporabimo za lokalizirano taljenje posameznih defektnih linij in njihovo spajanje v nove topološke objekte. Tak postopek sestavljanja je ekvivalenten rezanju in lepljenju trakov, ki jih ovijamo okrog različno razporejenih kroglic. Medtem ko lahko tri koloidne delce prepletemo zgolj na en sam način, se lahko štirje delci povežejo v vsaj tri različne 2D strukture. Iz trojčka najprej dobimo prepleten četverček, prikazan na sliki 20(d), kjer defektna zanka simetrično obkroži vse koloidne delce. Ta struktura je geometrijsko sestavljena iz dveh bočno zlepljenih parov osmic, topološko pa je enaka trivialnemu vozlu. Tako prepleteno strukturo lahko z optičnim preklapljanjem vmesnih defektnih pramenov pretvorimo v prekrizan koloidni četverček, ki je predstavljen na sliki 20(e). V tem primeru je notranjost prepletene konfiguracije geometrijsko ekvivalentna strukturi pletenice, vsak koloid pa je hkrati povezan z najbližjim in nasproti ležečim sosedom. Prvi topološko netrivialen primer prepletenosti štirih delcev je prikazan na sliki 20(f), kjer dve sklenjeni defektni zanki tvorita Hopfov splet. Osrednja koloidna delca sta med seboj povezana z dvema defektnima segmentoma, hkrati pa tudi z obema stranskima sosedoma. Iz tega sklepamo, da imajo defektne linije v geometriji zvitega direktorja precej prilagoditvenega prostora, zato lahko orientacijsko urejanje njihovih segmentov pomembno vpliva na število prepletenih zank, na lokalni tip povezanosti in posledično na topologijo kompleksno prepletenih vzorcev.

Na podlagi prikazanih primerov prepletenosti ugotavljamo, da so prepletene koloidne strukture v splošnem sestavljene iz različnih kombinacij osnovnih defektnih struktur osmice in pletenice, ki se prilagodijo ravninski razporeditvi koloidnih delcev. To nakazuje, da lahko zgolj določene prostorske konfiguracije defektnih zank zadovoljivo kompenzirajo inducirani topološki naboj, ki je neposredno vezan na število koloidnih delcev [85,121]. Zaradi lažje in dovolj natančne obravnave večjih 2D prepletenih struktur, se bomo v nadaljevanju osredotočili zgolj na periodične razporeditve delcev v obliki $p \times q$ koloidnih šablon, prikazanih na sliki 20(h-l). Začetna razporeditev šestih delcev podpira prepleteno strukturo Hopfovega spleta 2_1^2 , ki je topološko ekvivalentna strukturi na sliki 20(f). Kljub temu imata takšna topološka izomera različen topološki naboj, kar elegantno odpravi topološko degeneracijo struktur z različnim številom delcev. Pravo bogastvo topološke raznovrstnosti se prvič pokaže na zaporedju $p \times 3$ koloidnih šablon. Med prepletenimi defektnimi konfiguracijami prepoznamo vozle trilete 3_1 , Solomonov splet 4_1^2 , peterokraki vozle 5_1 in spleteno Davidovo zvezdo 6_1^2 . Vsi navedeni topološki objekti spadajo v družino vozlov in zank, ki jih lahko napnemo na površino torusa [151]. Ugotavljanje istovetnosti in topoloških lastnosti prepletenih zank si olajšamo z uporabo ravninske projekcije, ki jo najprej narišemo s programom KnotPlot [266] in jo potem preko zaporedja Reidemeistrovih premikov relaksiramo v ustrezno minimalno projekcijo. Ta postopek je eksplicitno prikazan na desni strani slike 20 za pet različnih topoloških konformacij. Vidimo, da kombinacije sodih p in lihih q ustrezajo dvokomponentnim torusnim spletom, medtem ko se lihe kombinacije p in q razpletejo v osnovne alternirajoče torusne vozle. Izraz 'alternirajoč' se nanaša na zaporedno izmenjavo nadvozov in

podvozov v minimalnih ravninskih projekcijah.

Topologijo vozlov in zank lahko popolnoma kontrolirano spreminjamo na izbrani koloidni šablони z nespremenjenim številom delcev. Na podlagi izkušenj in poznavanja raznovrstnih 2D prepletenih vzorcev ugotovimo, da lahko poljubno prepleteno stanje na $p \times q$ koloidni šablони prikažemo z ustrezno kombinacijo osnovnih Conwayevih determinant [151,177]. Na sliki 21 so prikazane tri osnovne determinante, obkrožene s črtkano črto in označene s simboli -1 , 0 in ∞ . Prva determinanta predstavlja negativno križišče dveh ravnih segmentov, ostali dve determinanti pa ustrezata vodoravni oziroma navpični mimobežni projekciji sosednjih segmentov. Med osnovnimi determinantami lahko enostavno preklapljam z operacijami rezanja, menjave in ponovnega lepljenja sosednjih defektnih pramenov, ki jih opravimo z natančnim spreminjanjem jakosti in lege optične pasti. Takšna lokalna rekonfiguracija defektnih zank pogosto povzroči spremembo topologije prepletenega vzorca. Desnoročni trilst na sliki 21(a) se zgolj ob zamenjavi označene determinante pretvori v dvokomponentni splet dveh zank, prikazan na sliki 21(b), ali v kompozitni vozle dveh levoročnih trilstov na sliki 21(c).



Slika 21: Conwayeve determinante so osnovni strukturni elementi rekonfigurabilnih defektnih vozlov in zank. Tri različne topološke konformacije se med seboj razlikujejo le znotraj obkroženih območij. Ta območja ustrezajo trem osnovnim dvokomponentnim determinantam, ki so označene s simboli -1 , 0 in ∞ . Posamezne determinante lahko preklapljam z optično pastjo, ki preko lokalno induciranega faznega prehoda prereže posamezne segmente in jih ponovno zlepi na drugačen način. Takšne operacije povzročijo strukturne spremembe, ki so pogosto povezane tudi s spremembo topologije prepletenih struktur: (a) desnoročni trilst 3_1^+ se pretvori v (b) dvokomponentni splet 6_3^2 z vodoravnim prerezom označenega križišča, nastali splet pa postane (c) kompozitni vozle $3_1 \# 3_1^-$ po menjavi mimobežnih determinant. Merilo na posameznih slikah ustreza $5 \mu\text{m}$.

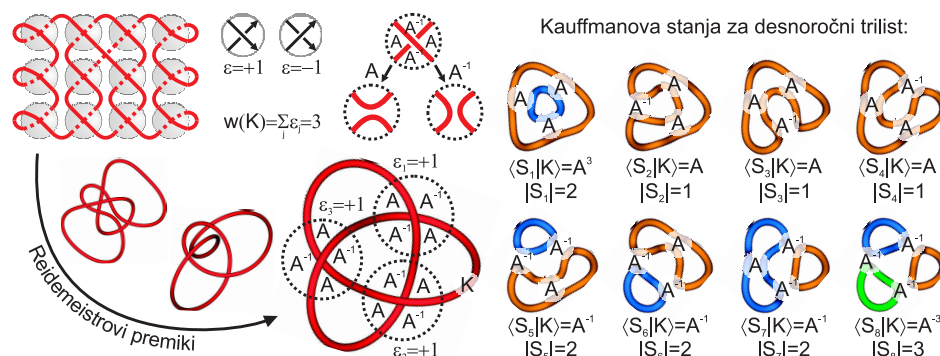
V nadaljevanju se osredotočimo na iskanje in prepoznavanje vseh možnih topoloških stanj na omejenih $p \times q$ koloidnih šablonah, pri čemer obravnavamo samo pravilno prepletene vzorce v dveh dimenzijah. Zadostni pogoj za takšno pletenje določa, da mora biti vsak posamezni koloidni delec povezan z dvema, tremi ali štirimi sosedi. Iz vseh dovoljenih planarnih kombinacij osnovnih determinant ugotovimo, da je število prepletenih topoloških konfiguracij določeno z enačbo:

$$N_{\text{konfiguracij}} = 4^{(p-1)} 3^{(p-1)(q-3)}, \quad p \geq 2, q \geq 3. \quad (6.28)$$

Zaradi izredno hitrega naraščanja števila konfiguracij se omejimo na relativno majhno množico stanj, ki jih določata $p, q \in \{2, 3, 4\}$. Klasifikacijo prepletenih vozlov in zank si olajšamo z uporabo polinomskih invariant, ki enoznačno določajo posamezne topološke strukture [149,151]. Minimalne projekcije topoloških objektov identificiramo s Kauffmanovim modelom stanj [156], ki nas pripelje do konstrukcije Kauffmanovega polinoma:

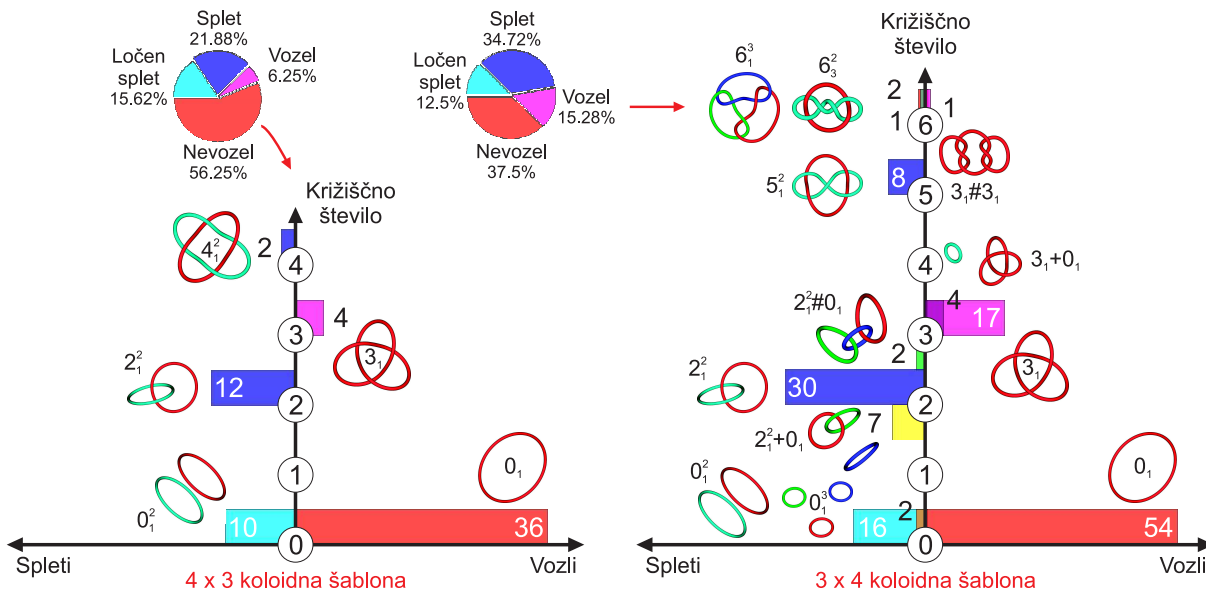
$$X(K) = (-A)^{-3w(K)} \sum_i \langle S_i | K \rangle (-A^2 - A^{-2})^{|S_i|-1}. \quad (6.29)$$

Pomen posameznih izrazov v zgornji enačbi in konkretni primer uporabe Kauffmanovega modela sta prikazana na sliki 22. Kauffmanov polinom desnoročnega trilsta je enak $A^{-7} - A^{-3} - A^5$.



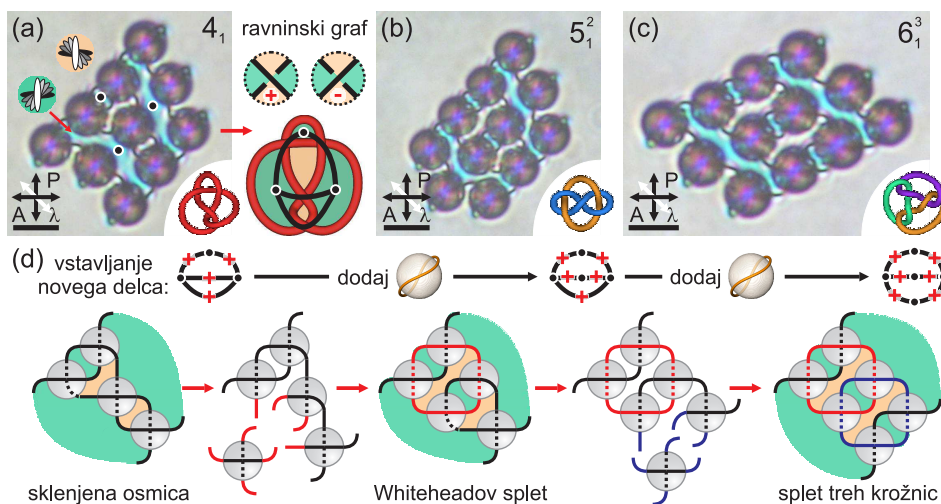
Slika 22: Konstrukcija Kauffmanovih stanj za desnoročni trilist. Fizikalna konformacija defektne zanke se preko zaporedja Reidemeistrovih premikov najprej relaksira v minimalno planarno projekcijo vozla. Izračuna se zvitost $w(K)$, vsako križišče posameznih segmentov pa se zgleda v eno izmed dveh stanj, A oziroma A^{-1} . Vse možne projekcije stanj določajo topološki tip vozla. $\langle S_i | K \rangle$ ustreza produktu vseh A in A^{-1} na izbranem križišču, medtem ko $|S_i|$ ustreza številu nespletenih krožnic v posameznem stanju.

Podoben postopek identifikacije topološkega tipa ponovimo za vsako posamezno prepleteno konfiguracijo. Izkáže se, da raznolikost topoloških struktur strmo narašča z dolžino defektnih linij in z velikostjo koloidnih šablon. Porazdelitvi topološko različnih konformacij vozlov in zank za primer dveh koloidnih šablon sta predstavljeni na sliki 23. Na manjši šablona prevladujejo preprosti objekti; več kot polovico primerov zastopa nevozel, pojavita se tudi dva najpreprostejša dvokomponentna spleta in osnovni trilist. Večja šablona postreže s pestrejšim naborom struktur. Med drugim opazimo Whiteheadov splet, splet treh krožnic ter primere kompozitnih vozlov in zank. Delež spletov preseže tretjino vseh možnosti, medtem ko ostaja delež vozlov relativno nizek in omejen. Raznolikost vzorcev je pogojena s tipično razporeditvijo osnovnih determinant vozlov, ki s svojo podobo močno spominjajo na znamenite keltske vozle in okraske [272]. V zvezi s tem se odpira kopica nerešenih vprašanj, ki se nanašajo na geometrijske lastnosti vzorcev, njihovo medsebojno povezanost, število spletenih komponent in posebej zahtevno topologijo.



Slika 23: Porazdelitev topoloških konfiguracij na dveh izbranih koloidnih šablonah. Vozli in zanke so razporejeni v skladu z naraščajočim križišnim številom. Kompleksnost in raznolikost topoloških objektov naraščata z dolžino prepletenih linij. Opazimo močno prevlado osnovnih vozlov in zank, ki predstavljajo več kot 90 % vseh spletov. Pojav kompleksnejših topoloških objektov je pogojen z velikostjo in obliko koloidne šablone.

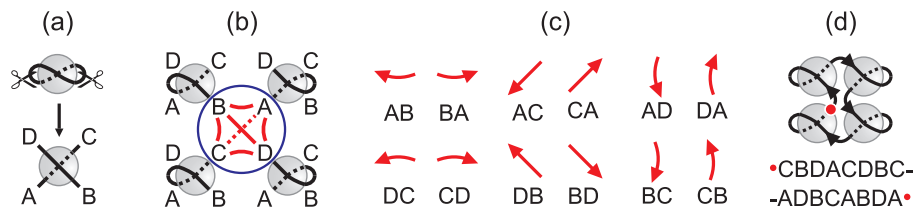
Naslednja zanimiva lastnost prepletenih koloidnih struktur v kiralnem nematskem polju je povezana z bistabilnimi orientacijami ograjenih zvojnih domen. V kolikor opazujemo prepletene strukture med prekrižanima polarizatorjema z vstavljenim optičnim kompenzatorjem, se levo-sučne in desnosučne domene pojavljajo v dveh različnih barvah, ki sta pogojeni s kotom in smerjo zasuka prepuščene svetlobe. Smer zvoja tekočerkristalnih plasti znotraj posameznega ograjenega območja pa je v glavnem pogojena z značilnim zvijanjem defektnih linij, ki ovijajo poljubno razporejene koloidne delce. Brez tega zvijanja v prostoru defektna linija namreč ne more ustvariti dovolj velikega topološkega naboja za ustrezno kompenziranje radialno induciranega naboja delcev. V tem primeru lahko namesto o zvijanju defektnih zank enakovredno govorimo o sukanju direktorskega polja znotraj območja, ki ga ta zanka ograjuje, zato so v tem pogledu efektivne zvojne domene različnih barv neposredna posledica ohranitve topološkega naboja. Nenazadnje imajo 2D prepleteni koloidni vzorci še prav posebno lastnost, saj se v teh strukturah efektivne zvojne domene med seboj izmenjujejo v pravilnem vzorcu, ki je skladen z ravninsko razporeditvijo koloidnih delcev; glej sliko 24.



Slika 24: Levo in desnosučne nematske domene se pojavljajo v dveh različnih barvah, zeleni in sivi, ko jih opazujemo med prekrižanima polarizatorjema z vstavljenim optičnim kompenzatorjem. Barvi se spontano izmenjujeta v skladu z lokalno smerjo zasuka tekočerkristalnih molekul. (a-c) Iz barvnih fotografij koloidnih struktur lahko enostavno sestavimo ravninske grafe, ki ustrezajo topološkemu tipu prepletenih zank. Na zeleno obarvana področja postavimo oglišča, ki jih nato med seboj povežemo preko vmesnih križišč. Glede na vrsto križišča lahko vsaki povezavi pripišemo tudi predznak, ki nam določi končno podobo grafa. V primeru osnovnih vozlov in zank imajo vse povezave enak predznak. (d) Z dodajanjem novih delcev v obstoječo koloidno strukturo se število efektivnih domen spremeni, kar se neposredno opazi tudi v sami strukturi grafa. Posamezni segmenti se povežejo na nov način, s čimer spremenijo število zank in topologijo objekta. Merilo na posameznih slikah ustreza $5\ \mu\text{m}$.

Ta posebna lastnost alternirajočih domen omogoča neposredno povezavo s teorijo grafov [149,151]. Prepletene koloidne strukture namreč predstavljajo naravno ogrodje za konstrukcijo senčenih ravninskih projekcij, iz katerih enostavno izluščimo pripadajoč ravninski graf. Postopek konstrukcije grafa je prikazan in razložen na sliki 24(a-c). Topologijo prepletenih struktur lahko spreminjamo tudi z dodajanjem oziroma odvzemanjem delcev. Primer na sliki 24(d) kaže, da vsak dodani koloid prispeva dodatno oglišče in pozitivno predznačeno povezavo v pripadajočem grafu. Prikazani grafi nam lahko velikokrat olajšajo prepoznavanje sorodnih planarnih projekcij vozlov in zank, saj se rotacijske in zrcalne simetrije struktur preslikajo na obliko grafa. Na ta način enostavneje identificiramo topološke izomere, zahtevnejše primere pa moramo najprej poenostaviti z Reidemeistrovimi premiki na grafih. Učinkovitega algoritma, ki bi lahko razvozlal ali je poljubna projekcija vozla ekvivalentna trivialnemu vozlu pa zaenkrat ne poznamo niti v teoriji grafov [151].

Doslej smo se v glavnem ukvarjali z identifikacijo in klasifikacijo posameznih prepletenih defektnih konfiguracij, sedaj pa se bomo posvetili ugotavljanju strukturnih podobnosti in relacij, s katerimi lahko opišemo posamezne strukturne spremembe na $p \times q$ koloidni šabloni. Čeprav nam grafična predstavitev spleto ponuja veliko geometrijskih in topoloških informacij, je včasih dobrodošel tudi znakovni zapis strukture v prostoru. Edinstven primer najdemo v naravi v obliki genskega zapisa informacij, ki ustreza zaporedju štirih nukleotidov (A = adenin, C = citozin, G = gvanin, T = timin), razporejenih v obliki dvojne vijačnice DNK. Na podoben način lahko priredimo zaporedje črk tudi gradnikom naših prepletenih struktur. Za bazo izberemo koloidni delec, na katerem se zmeraj križata dva defektna segmenta. Ta segmenta na robovih prerežemo in dobimo štiri presečišča, katerim pripišemo ustrezen nabor črk A, B, C in D; glej sliko 25(a). Ker lahko koloidne delce povezujemo v dveh dimenzijah na le nekaj izbranih načinov, ki ustrezajo trem osnovnim determinantam spleto, je število meddelčnih povezav omejeno na šest segmentov, prikazanih z rdečo barvo na sliki 25(b). Tem segmentom pripišemo orientacijo, ki jo določimo z ustreznim parom črk. Tako dobimo 12 osnovnih orientiranih segmentov s katerimi lahko opišemo poljubno 2D prepleteno defektno konfiguracijo; glej sliko 25(c). Preprost primer črkovnega zapisa prepletene topološke strukture je prikazan na sliki 25(d).

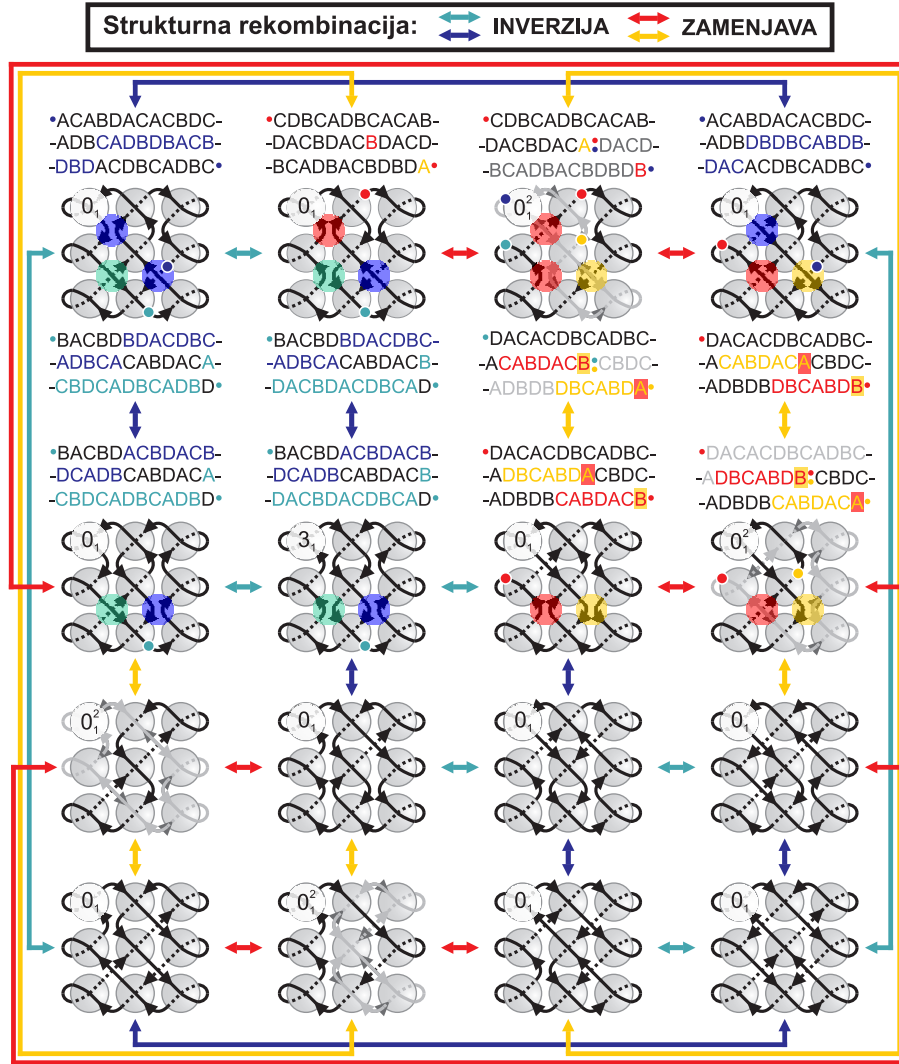


Slika 25: Orientacijsko kodiranje defektnih segmentov. (a) Kot osnovo izberemo izoliran defektni obroč, ki ga prerežemo na dveh koncih. Štirim prostim pramenom priredimo zaporedje črk A, B, C in D. (b) Vse 2D prepletene strukture lahko povežemo s kombinacijami treh osnovnih determinant, ki jih sestavlja šest defektnih segmentov. (c) Tem šestim segmentom določimo smer, ki ustreza izbranemu paru črk. (d) Potek prepletene defektne zanke opišemo s periodičnim zaporedjem črk. Začetek zaporedja je označen s poljubno izbrano točko, smer zapisa pa nakazujejo puščice.

Orientacijsko kodiranje prepletenih defektnih linij nam olajša raziskovanje strukturnih prehodov med geometrijsko sorodnimi vzorci na $p \times q$ koloidnih šablonah. Prednost sistema šablon je v tem, da imamo znan in dobro definiran nabor topoloških konfiguracij, ki jih lahko enostavno opišemo in medsebojno spreminjamo. Za primer smo izbrali 16 prepletenih konfiguracij na 3×3 koloidni šabloni, ki so nazorno ilustrirane na sliki 26. Vsaka konfiguracija je opremljena z Rolfsenovo notacijo [174], ki razkriva, da imamo zbranih 11 nevozlov 0_1 , štiri ločene splete 0_1^2 in en trilesti vozle 3_1 . Posameznemu prepletu najprej določimo smer, nakar izberemo izhodišče in zapišemo ustrezno periodično zaporedje črk vzdolž celotnega poteka zanke. Dvema zankama ustrežata dve ločeni zaporedji.

V nadaljevanju nas zanimata dve sosednji konfiguraciji, ki sta med seboj povezani z dvojno puščico določene barve. Ta puščica označuje strukturni prehod, ki je ponazorjen z barvnim krogcem na sami koloidni strukturi in ki ustreza zamenjavi izbranih osnovnih determinant. V teh primerih gre za menjavo križišč in navpično odprtih determinant, ki smo jih v eksperimentih izvedli z uporabo optične pasti. Izkaže se, da lahko vse strukturne prehode med sosednjimi prepletenimi konfiguracijami opišemo zgolj s kombinacijo dveh osnovnih operacij. Zaradi podobnosti z operacijami, ki jih na DNK izvajajo nekateri encimi [158,162,273], imenujemo to vrsto operacij *strukturna rekombinacija*. Prvi primer rekombinacije predstavlja *inverzija*, ki ustreza inverziji dela črkovnega zaporedja oziroma obrnitvi orientacije na izbranem segmentu. Na sliki 26 je označena z zeleno oziroma modro barvo. Enako obarvana kosa dveh sosednjih zaporedij se torej preslikata eden v drugega z uporabo inverzije, medtem ko ostali deli zaporedja ostanejo nespremenjeni. Tak strukturni prehod lahko povzroči tudi spremembo topologije, npr. vozle se pretvori v nevozle, vendar se pri tem ohrani število prepletenih zank. Drugi tip strukturne

rekombinacije imenujemo *zamenjava*, saj pride v tem primeru do zamenjave segmentov, ki pripadata dvema različnima zankama. Pri tem se orientacija zank ohrani, njihovo število pa se poveča oziroma zmanjša za ena. V črkovnem zapisu se ta operacija zrcali v dveh obarvanih koščkih zaporedja, ki po strukturnem prehodu zamenjata svoji mesti. Na sliki 26 so zamenjave označene z rdečo oziroma rumeno barvo.



Slika 26: Pregled strukturnih prehodov med sosednjimi prepletenimi konfiguracijami na 3×3 koloidni šabloni. Vse strukturne prehode opišemo zgolj z dvema rekombinacijama defektnih segmentov. V primeru inverzije se izbranemu segmentu obrne orientacija, kar se zrcali tudi v inverziji dela črkovnega zaporedja. V primeru zamenjave se orientacija zank ohranja, spremeni pa se njihovo število in posledično topološki tip. Ta operacija se jasno pokaže z zamenjavo dveh obarvanih koščkov črkovnega zaporedja, ki po strukturnem prehodu zamenjata svoji mesti. Posamezni prehodi so označeni z barvnimi puščicami, mesto spremembe je nakazano z barvnim krogcem, začetek črkovnega zaporedja pa z obarvano točko. Zaradi preglednosti je prikazan samo del črkovnih zaporedij.

Število možnih strukturnih prehodov je povezano z obliko in velikostjo koloidne šablone, ki določa ravninsko razporeditev osnovnih determinant. Na 3×3 šabloni imamo na voljo štiri različna mesta, na katerih preklapljamemo med dvema (-1 in ∞) osnovnima determinantama. V splošnem je število strukturnih rekombinacij na $p \times q$ šabloni določeno z enačbo:

$$N_{\text{rekombinacij}} = N_{\text{konfiguracij}}(p-1)(1+(q-3)), \quad p \geq 2, q \geq 3, \quad (6.30)$$

pri čemer je $N_{\text{konfiguracij}}$ določen z enačbo (6.28). Na osnovi strukturnih rekombinacij lahko

izvedemo preprosto klasifikacijo topoloških objektov, ki so med sabo povezani z določenimi strukturnimi prehodi. Na majhnih šablonah s $p, q \in \{2, 3, 4\}$ se izkaže, da lahko poljubno prepleteno konfiguracijo zelo hitro razpletemo v trivialni vozle, saj sta za to potrebni največ dve zaporedni rekombinaciji. Podrobnejša analiza obravnavanih vozlov in zank bi morala vključevati še metode diferencialne geometrije in algoritem pletenja kit, ki bi olajšali identifikacijo in samo klasifikacijo prepletenih vzorcev.

Z aplikativnega vidika so nematske pletenice potencialno uporabne kot topološke tarče za lovljenje in urejanje dispergiranih nanodelcev ter makromolekul. Podobni principi samourejanja so bili že prikazani pri stabilizaciji holesteričnih modrih faz [92,95], vendar v teh primerih ni šlo za dovršeno organizacijo defektnih struktur. Zanimiva topologija spletenih vzorcev bi lahko omogočila tudi raziskave reptacije polimernih filamentov in nadzorovan transport mikrododelcev med ograjenimi zvojnimi domenami. Nenazadnje pa so odkrite prepletene defektne strukture eden izmed najatraktivnejših in topološko najbogatejših modelskih eksperimentalnih sistemov, ki omogočajo raznovrstne aplikacije matematične teorije vozlov.

Zaključek

Doktorsko delo obravnava eksperimentalne raziskave meddelčnih interakcij in sestavljanje novih koloidnih struktur v tankih plasteh nematskega tekočega kristala z uporabo optične pincete. Tema doktorskega dela je posvečena odkrivanju novih principov samoorganizacije mikroskopskih delcev v anizotropnih tekočinah, ki lahko vodijo do periodično urejenih 2D koloidnih struktur. Tehnologije prihodnosti namreč zahtevajo vse bolj kompleksne kompozitne materiale s periodičnimi strukturami v mikrometrskem in nanometrskem območju, ki obenem omogočajo nadzorovano uravnavanje elektro-optičnih in mehanskih lastnosti. Delo je v veliki meri potekalo vzporedno z numeričnim modeliranjem obravnavanih problemov, kar je omogočilo kvantitativno kritično primerjavo eksperimentalnih in teoretičnih rezultatov.

Pričujoče doktorsko delo temeljito obdela sestavljanje 2D koloidnih struktur v uniformnem in kiralnem nematskem polju z optično pinceto. V okviru tega dela smo podrobneje raziskali jakost meddelčnih potencialov, (meta)stabilnost koloidnih struktur, sestavljanje periodičnih 2D koloidnih kristalov, vpliv inducirane nereda na defekte v prepletenih koloidnih strukturah, pretvorbe med singularnimi in nesingularnimi topološkimi defekti ter nastanek kompleksnih topoloških struktur v obliki defektnih vozlov in zank.

V prvem delu so predstavljeni rezultati, ki smo jih dosegli skupaj s sodelavci v prvih dveh letih mojega podiplomskega izobraževanja. Čeprav so k pobudi in izvedbi teh eksperimentov bistveno prispevali sodelavci, je to sodelovanje pomembno vplivalo na razvoj mojih lastnih idej, ki so kasneje privedle do glavnih dosežkov doktorskega dela. Najprej smo v geometriji planarne tekočerkristalne celice iz posameznih homeotropnih delcev sestavili koloidne strukture na osnovi elastičnih dipolov in kvadrupolov. Obravnavali smo pare delcev in pri tem ugotovili, da dva vzporedno orientirana dipola tvorita linearno verigo v smeri daljnega direktorja, dva dipola z nasprotno usmerjenima točkovnima defektoma pa se privlačita bočno. Kvadrupolni par ima dve simetrični, bočno stabilni legi, zveznica med delcema pa je postavljena skorajda pravokotno na smer daljnega direktorskega polja. Pare delcev smo nadalje sestavili v linearne dipolne in zlomljene kvadrupolne verige. Pri večjih koncentracijah delcev smo opazili spontano urejene 2D koloidne skupke, ki smo jih z optično manipulacijo posameznih delcev sistematično uredili v periodične 2D nematske koloidne kristale. Odkrili smo dva tipa kristalov, dipolne in kvadrupolne, ki se razlikujeta po obliki kristalne mreže in po jakosti meddelčnih interakcij. Dipolni koloidni kristal je sestavljen iz antiparalelnih dipolnih verig, ki se bočno privlačijo in tvorijo stabilno periodično strukturo. Kvadrupolni koloidni kristal je zaradi anizotropne meddelčne interakcije vezan precej šibkeje in kmalu razpade na skupke posameznih kvadrupolnih verig. Vezavni mehanizem, ki določa natančen pozicijski in orientacijski red v nematskem koloidnem kristalu, je v obeh primerih enak. Zanj so odgovorne meddelčne strukturne sile, ki nastanejo zaradi zmanjševanja

elastičnih deformacij nematskega polja. To odkritje predstavlja prvi primer eksperimentalne realizacije koloidnih kristalov, ki jih je mogoče stabilizirati zgolj z elastičnim prilagajanjem gostiteljskega medija. V nadaljevanju smo poskušali postopek sestavljanja avtomatizirati z uporabo zunanega električnega polja, ki nam je omogočilo masovni transport in kristalizacijo delcev na makroskopskem nivoju. Žal se je tak poskus urejanja izkazal za preveč robustnega, saj z njim ni mogoče zagotoviti gradnje pravilnih koloidnih struktur in ustrezne stabilnosti po izklopu zunanega električnega polja. Pri določenih debelinah eksperimentalne celice smo opazili soobstoj dipolnih in kvadrupolnih delcev, ki smo jih lahko medsebojno preklapljali s spreminjanjem ograjenosti in uporabo lokalno inducirane faznega prehoda. To opažanje je kasneje privedlo do sestavljanja množice mešanih dipolno-kvadrupolnih nematskih koloidnih kristalov.

Na podlagi rezultatov numeričnih simulacij smo uvedli nov vezavni mehanizem, ki temelji na nenadnem upadu temperature iz izotropne v nematsko fazo, pri čemer se tvorijo kompleksne metastabilne koloidne konfiguracije, v katerih delokalizirane hiperbolične defektne linije prepletejo večje število delcev. Nenaden dvig oziroma padec temperature v izbranem območju tekočeh kristalne plasti dosežemo z optično pinceto, ki omogoča lokalizirano gretje vzorca. Pri tem nastanejo novi, topološko stabilni objekti, ki jih imenujemo nematske pletenine. Za primer koloidnih parov smo eksperimentalno potrdili napovedane prepletene strukture osmice, pletenice in prepletenega točkovnega defekta. Osmica in pletenica spontano zlomita zrcalno simetrijo direktorskega polja in sta zato kiralna objekta. Meddelčni potencial v prepletenih strukturah je izredno močan in strunast, kar v grobem zagotavlja prostorsko neodvisno silo med delci. Prepletenost delcev z defektnimi linijami smo posplošili tudi na linearne verige. Verigo osmic tvori ena sama defektna zanka s topološkim nabojem, ki je nasprotno enak inducirane naboju delcev v verigi. Pojav prepletenosti smo naknadno izkoristili za povzročanje elastičnih deformacij direktorskega polja na različnih prostorskih skalah z delci različnih velikosti. Takšne deformacije ustvarijo hierarhičen meddelčni potencial, kjer večji delci diktirajo urejanje manjših delcev v t.i. koloidnih superstrukturah.

V osrednjem delu doktorske disertacije so predstavljeni glavni rezultati, ki so razdeljeni v tri ločene sklope. Najprej smo pokazali, da simetrija elastične deformacije gostiteljskega medija ni izključno odvisna od oblike dispergiranih delcev, temveč zgolj od kombinacije robnih pogojev na ograjajočih površinah. Koloidni delci v obliki palčk so še posebej zanimivi, ker zlomijo zrcalno simetrijo direktorskega polja, kar povzroči silo in navor na ravnovesno orientacijo delcev. V eksperimentih smo se osredotočili na topološko analizo defektnih konfiguracij v neposredni okolici homeotropnih mikropalčk, ki smo jih ogradili z uniformnim nematskim poljem. Opazili smo dva pričakovana tipa deformacije, dipolno in kvadrupolno, ki sta bila jasno razvidna že iz same orientacije delcev. Interakcije med posameznimi koloidnimi pari in izmenično preklapljanje med obema defektnima konfiguracijama smo podrobneje raziskali z optično pinceto. Ugotovili smo, da sta tip in jakost interakcij dveh mikropalčk povsem primerljiva z interakcijami dveh koloidnih verig, sestavljenih iz kroglic podobne velikosti. Ravnovesne konfiguracije dipolnih in kvadrupolnih parov mikropalčk so prav tako zelo podobne parom sferičnih koloidov, kar potrjuje napovedi nedavnih teoretičnih raziskav. Izvedeno eksperimentalno delo je vzbudilo zanimanje drugih raziskovalnih skupin, ki so v kratkem času pokazale, kako lahko v anizotropnih topilih preko oblike delcev kontroliramo tudi tip meddelčnih interakcij in s tem prispevamo k nastanku množice novih koloidnih struktur.

V nadaljevanju smo se osredotočili na energijsko stabilizacijo različnih koloidnih struktur v neuniformnem kiralnem direktorskem polju. Uporabili smo geometrijo 90° zvojne nematske celice, ki povzroči spremembo organizacije topoloških defektov in zamenja relativno stabilnost oziroma metastabilnost prepletenih in neprepletenih defektnih konfiguracij. Kiralno nematsko polje namreč močno zavre samosestavljanje linearnih dipolnih verig, obenem pa omogoči spontano pretvorbo točkovnih defektov v pobegle hiperbolične defektne obroče, ki z nesingularnim direktorskim poljem povežejo delce v topološko neločljive pare z linearno odvisnim meddelčnim potencialom. Opazili smo dva tipa defektnih obročev, ki ustrezata različnim smerem pobega

direktorskega polja v tretjo dimenzijo. V izbrani zvojni domeni imajo levo oziroma desnoročni pobegli defektni obroči različne vezavne energije, pri čemer je kombinacija nasprotne smeri pobega in zunanega zvoja energijsko bistveno ugodnejša. Zato lahko geometrijo zvojne celice uporabimo kot mehanizem za kiralno selektivnost dispergiranih delcev. Razen tega smo z optično pinceto uspeli sestaviti množico novih 2D nematskih koloidnih kristalov s poljubno ročnostjo. Ti kristali imajo poleg zanimivih strukturnih in optičnih lastnosti tudi izjemen elastomehanski odziv, ki pod vplivom zunanega električnega polja ustreza pojavu superelastičnosti.

Ugotovili smo tudi mnoge podobnosti med koloidnimi strukturami, ki so vezane s pobeglimi defektnimi obroči in tistimi, ki so prepletene z delokaliziranimi defektnimi linijami. V obeh primerih defekti stabilizirajo topološko neločljive objekte, ki jih lahko razumemo kot osnovne gradnike kompleksnejših koloidnih struktur. Preprosto orientacijsko urejanje na podlagi okoliških motenj elastičnega medija je v tem primeru nadgrajeno s spajanjem sosednjih defektnih zank, ki nosijo večkratnike topološkega naboja posameznih delcev in v nematiku brez ustrezne stabilizacije z delci ne morejo obstajati. Na paru delcev pokažemo, da ima struktura osmice najnižjo prosto energijo, tudi če jo primerjamo z neprepleteno strukturo dveh kvadrupolnih Saturnovih obročev. Razen tega lahko strukturo osmice z relativno spremembo položaja delcev reverzibilno pretvorimo v pobegli defektni obroč, kar odpira množico topoloških prehodov med pobeglimi in prepletenimi defektnimi konfiguracijami.

Geometrija zvojne celice omogoča tudi energijsko ugodnejše sestavljanje prepletenih 2D koloidnih struktur. Te strukture predstavljajo vrhunec doktorskega dela, saj smo z njimi odkrili neomejeno množico vozlov in spletov, ki nastanejo kot posledica spretne manipulacije ograjenega direktorskega polja. Objekti, ki tvorijo vozle in splete so delokalizirane hiperbolične defektne linije, ki na raznovrstne načine prepletajo koloidne delce. Dosedanji poskusi vzlanja filamentov v bioloških in mehkih sistemih na (pod)mikrometrskem nivoju so namreč izjemno redki in omejeni zaradi majhnosti raziskovanih objektov ter ogromnega števila slabo definiranih topoloških konformacij. V nasprotju s temi sistemi je naš eksperimentalni pristop pletenja vozlov iz topoloških defektov v anizotropnem sredstvu relativno preprost, dobro definiran in enostavno ponovljiv. Sistematična analiza prepletenih vzorcev z metodami matematične teorije vozlov je razkrila osnovne strukturne elemente, ki jih lahko poljubno rekonfiguriramo z uporabo optične pasti. Mnogo netrivialnih konfiguracij spada v družino torusnih vozlov in zank, razen teh pa se pojavljajo tudi alternirajoči sebi zrcalni vozli in kompleksni večkomponentni spleti. Že na relativno majhnih koloidnih šablonah nam je uspelo identificirati okrog 20 različnih osnovnih in sestavljenih vozlov oziroma spletov, njihova kompleksnost pa se s širjenjem konformacijskega prostora le izdatno povečuje. Raziskali smo tudi različne strukturne sorodnosti med posameznimi spletenimi vzorci in ugotovili, da lahko poljuben vzorec pretvorimo v nek drug vzorec zgolj z uporabo dveh preprostih strukturnih rekombinacij. Prvi primer rekombinacije predstavlja inverzija, ki obrne orientacijo ustreznega segmenta, pri čemer se ohrani število spletenih komponent, lahko pa se spremeni topološki tip objekta. Drugi tip strukturne rekombinacije imenujemo zamenjava, saj pride v tem primeru do zamenjave segmentov, ki pripadata dvema različnima komponentama spleta in s tem do nujne spremembe topološkega tipa. Pri tem se orientacija zank ohrani, njihovo število pa se poveča oziroma zmanjša za ena. Pričakujemo, da lahko nadaljnje raziskave strukturnih prehodov razkrijejo splošna pravila identifikacije in klasifikacije poljubno prepletenih vzorcev na 2D koloidnih šablonah, pri čemer so lahko v veliko pomoč lokalne geometrijske in globalne topološke invariante defektnih zank. Nenazadnje so odkriti vozli in spleti v kiralnem nematskem polju eden izmed topološko najbolj bogatih modelskih sistemov, ki omogočajo ogromno aplikacij matematične teorije vozlov.

Nematski tekočokristalni koloidi so novi kompozitni materiali z izredno zanimivimi elektrooptičnimi in elastomehanskimi lastnostmi, ki se pojavljajo v obliki mnogih fascinantno urejenih struktur. Za njihov obstoj so odgovorne strukturne sile tekočega kristala, ki se pojavijo zaradi elastičnih deformacij molekularnega polja med dispergiranimi koloidnimi delci. Vezavni potenciali mikrometrskih delcev so izjemno močni in dosegajo vrednosti nekaj $1000 k_B T$. Mehanizem

sestavljanja temelji na minimizaciji motenj v orientacijskem redu nematika in omogoča izredno privlačno metodo samosestavljanja, ki ni posebej odvisna od materialnih lastnosti posameznih komponent. Postopek sestavljanja lahko enostavno nadziramo z uporabo različnih zunanjih polj, med katerimi izstopa tehnika manipuliranja koloidnih delcev z optično pinceto. Prav tako ni posebnih omejitev za miniaturizacijo nastalih struktur, kar pomembno razširi možnosti uporabe njihovih izrednih optičnih lastnosti. Sicer pa je glavni aplikativni potencial tekočerkristalnih koloidov še posebej odvisen od razvoja eksperimentalnih metod, ki bi omogočile preprosto sestavljanje pravilnih 3D koloidnih struktur v velikem obsegu.

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AUTHORSHIP DECLARATION

I the undersigned UROŠ TKALEC declare herewith that:

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