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Luxembourg, May 10-12, 2017

On the physics, chemistry and applications of cholesteric lyotropic liquid crystals developing in colloidal suspension of chiral nanorods, such as nanocrystals of cellulose or chitin, filamentous viruses or carbon nanotubes.



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Welcome

Dear colleagues,

It is our pleasure to welcome you to *Twisted*, a two-day conference on the physics, chemistry and applications of cholesteric lyotropic liquid crystals developing in colloidal suspensions of chiral nanorods, held here, on the campus Limpertsberg of the University of Luxembourg.

We are very happy to bring together experts in experimental, computational and theoretical fields of liquid crystal research.

We thank you for your participation in this event and we hope that you enjoy the conference!

Members of the organization committee

Jan Lagerwall, Tanja Schilling, Zornitza Tosheva, Christina Schütz, Camila Honorato-Rios and Anja Kuhnhold

Useful Information

Map of the center of Luxembourg



Workshop venue

From the railway station or the city center (Hamilius) to the University, you can take bus 2 or 4 (same itinerary) and exit at the terminus "L.T. Michel Lucius". You can buy the ticket from the driver ($2\epsilon/2h$ or $4\epsilon/day$). Going out of the bus (quai 101), go on your left hand side and take the street on the right (Rue Guillaume Capus). The entrance of the Campus is a 100 meter away.



The conference will be held in room BS003 located in the "Bâtiment des Sciences". Walking lunches and coffe breaks will be served at several locations indicated in the floor map below.



Poster sessions

The poster sessions will be held on 11th and 12th May 2017 in the coffee break area (see map above) during the lunch breaks. Poster must be mounted before the start of the workshop on Thursday morning, and taken down during the last coffee break on Friday.

Internet conection

The wifi access for the workshop will be available from May 10th to May 12th.

Password: Twisted@UL2017

Social dinners

The Welcome dinner will be served at *Brasserie du Cercle* on 10th May 2017 starting at 8 pm and the Farewell dinner will be served at *Big Beer Company* on 12th May 2017 starting at 8 pm.

In case you forgot your menu choices, you can see them on the back of your badge.

Restaurants

Luxembourg offers a variety of cuisines, like French, Portuguese or German. You will find lots of (takeaway) restaurants going down the Avenue Pasteur, 15 minutes walking distance from the Campus.

For dinner we recommend the restaurants located in the city center.

Program

Wednesday 10th of May (2017)

13:00 – 17:00 Registration (Campus Limpertsberg, secretaries offices)

20:00 Meet-together dinner (City center, Brasserie du Cercle)

Thursday 11th of May (2017)

8:15 - 8:45	Registration (Lecture hall)
8:45 - 9:00	Welcome and Opening address by UL president Prof. Rainer Klump
	Session 1: Advanced materials derived from chiral nanorods
9:00 - 9:50	Keynote: Mark MacLachlan University of British Columbia, Vancouver, Canada New Photonic Materials from Cellulose Nanocrystal Templating
9:50 - 10:30	Invited: Maria-Helena Godinho Universidade Nova de Lisboa, Lisbon, Portugal From cotton to advanced electro- tunable photonic materials
10:30 - 11:00	Bruno Frka-Petesic University of Cambridge, United Kingdom cholesteric self-assembly of a cellulose nanocrystal suspension in a rinking microdroplet
11:00 - 11:30	Coffee break

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11:30 – 12:10 Invited: Olli Ikkala Aalto University, Espoo, Finland Chiral assemblies along cellulose nanocrystals

12:10 – 12:40 Emily D. Cranston
 McMaster University, Hamilton, ON, Canada Magnetic Alignment of Cellulose
 Nanocrystals in Suspension and in Hydrogels: Kinetics and Order Parameters

- 12:40 13:10 Virginia A. Davis Auburn University, AL, USA Phase Behavior, Rheology, and Solidified Microstructure of Aqueous Cholesterogenic Nanomesogen Systems
- 13:10 14:30 Walking lunch + poster session

Session 2: Theory and simulations of cholesteric phases

- 14:30 15:20 Keynote: Mark Wilson
 Durham University, Durham, UK Spontaneous formation of chiral systems from achiral liquid-crystalline molecules
- 15:20 16:00 Invited: Claudio Zannoni University of Bologna, Bologna, Italy Is chirality always needed to obtain twisted molecular organizations?
- 16:00 16:30 Akihiko Matsuyama
 Kyushu Institute of Technology, Fukuoka, Japan Field-induced twist-bend distortion in mixtures of chiral and achiral molecules
- 16:30 17:00 *Coffee break*
- 17:00 17:40 Invited: Paul van der SchootEindhoven University of Technology, The Netherlands Percolation of Hard Rodsin the Uniaxial Nematic Phase
- 17:40 18:10 Maxime Tortora
 University of Oxford, United Kingdom Density-functional theory for cholesteric phases of realistic flexible particles
- 18:10 18:40 Cristano De Michele
 "Sapienza" Università di Roma, Rome, Italy Hierarchical propagation of chirality through reversible polymerization: the cholesteric phase of DNA oligomers

Friday 12th of May

8:30 – 9:00 Registration (Lecture hall)

Session 3: Chiral nanorod suspensions: from particle tuning to self-assembly

9:00 – 9:50 Keynote: Derek Gray McGill University, Montreal, Canada Twisted Cellulose

9:50 – 10:30 Invited: Henricus H. Wensink CNRS, Université Paris-Sud, Université Paris-Saclay, France Compensated cholesterics of helical mesogens: insights from simple microscopic models

- 10:30 11:00 Joshua Berryman University of Luxembourg Kinetic Control of Chiral Self Assembly
- 11:00 11:30 *Coffee break*
- 11:30 12:10 Invited: Zvonimir Dogic Brandeis University, Waltham, MA, USA Rigid filaments with varying chirality and tuneable shape
- 12:10 12:40 Eric Grelet CNRS & University of Bordeaux, France Rod-like Viruses as Model System for Studying Chirality Amplification in Colloidal Liquid Crystals
- 12:40 13:10 Giuliano Zanchetta University of Milano, Italy Twist and shout: chirality amplification and fluctuation modes in the cholesteric phase of short DNA
- 13:10 14:30 Walking lunch + poster session

Session 4: The route to applications

- 14:30 15:20 Keynote: Silvia VignoliniCambridge University, Cambridge, UK Cellulose photonics: from nature to applications
- 15:20 16:00 Invited: Lennart Bergström Stockholm University, Stockholm, Sweden Single-Fibril Properties and Assembly of Nanocellulose-Based Hybrid Materials
- 16:00 16:30 Dhriti Nepal Air Force Research Laboratory, Wright Patterson Air Force Base, Ohio, USA Engineering of Chiral Phases from Cellulose Nanocrystals: Effect of CNCs Dimension and SO₃ content
- 16:30 17:00 *Coffee break*
- 17:00 17:40 Invited: Youssef Habibi
 Luxembourg Institute of Science & Technology, Luxembourg Organized thin
 films of cellulose nanocrystals: From model to optically active films
- 17:40 18:10 Laurent Heux CERMAV-CNRS, Grenoble, France Dynamically controlled iridescence of cellulose nanocrystal assemblies with electric field
- 18:10 18:40 Qi Zhou

Royal Institute of Technology, Stockholm, Sweden Flexible Chiral Nematic Cellulose Nanocrystals Film with Brilliant and Tunable Structural Color

20:00 – Farewell dinner (City Centre, *Big Beer Company*)

Oral Lectures

Session 1:

Advanced materials derived from chiral nanorods

New Photonic Materials from Cellulose Nanocrystal Templating

Mark J. MacLachlan

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Complex supramolecular structures are abundant in nature. Spider silk and nacre, for example, are two natural materials whose impressive mechanical properties arise from their hierarchical structures. Inspired by these and other examples, chemists are turning to natural materials to construct new substances with fascinating properties.

Cellulose nanocrystals (CNCs) obtained from biomass self-assemble into a helicoidal arrangement that mimics the organization of mesogens in chiral nematic (cholesteric) liquid crystals.^[1,2] This organization can be used as a template to construct composite films of CNCs and other materials, such as silica^[3] (Figure 1) and polymers.^[4] By removing one component – either the CNCs or the matrix – one is left with a mesoporous film with a chiral nematic arrangement of holes.^[5]

In this talk, I will discuss our recent developments in this area, templating new materials with photonic properties.



Figure. Photograph of chiral nematic mesoporous silica films (source: reference 3). The coin is for scale.

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- 2. J.-F. Revol, L. Godbout, D. G. Gray, J. Pulp Pap. Sci., 24, 146-149 (1998).
- 3. K. E. Shopsowitz, H. Qi, W. Y. Hamad, M. J. MacLachlan, Nature, 468, 422-425 (2010).
- M. K. Khan, A. Bsoul, K. Walus, W. Y. Hamad, M. J. MacLachlan, Angew. Chem. Int. Ed., 54, 4304-4308 (2015).
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From cotton to advanced electro-tunable photonic materials

<u>Maria Helena Godinho</u>, Pedro Almeida, Nuno Monge, Ana Almeida, Susete Fernandes CENIMAT/I3N, Departamento de CiÃ^ancia dos Materiais, Faculdade de CiÃ^ancias e Tecnologia, FCT, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal

Plants produce a large variety and amount of cellulose based-structures forming meso, micro and nano buildings with unique features and complex shapes. In this work we address the use of cellulose nanocrystals, isolated from cotton micro fibers, to produce, from liquid crystalline water cellulose nanocrystals solutions (iridescent solid film in Figure 1 a., b. and c.), responsive photonic films (Figure 1 d., e. and f.). The unique material photonic properties are acquired by the combination of the chiral solid iridescent cellulose films characteristics, with the responsiveness, to an electric field or temperature, of a nematic liquid crystal [1]. Cellulose-inspired responsive materials have a significant potential for the production of lightweight, low cost soft materials with impact on intelligent textiles, energy generation as well as in bio-medical and biosensing devices.



Figure. Photographs of cellulose nanocrystals (CNCs) iridescent solid film (a., b. and c.) and CNCs film with nematic liquid crystal (5CB) (d., e. and f.), observed with white light and circularly polarized light, showing different reflection responses similar to *Plusiotis batesi* and *Plusiotis resplendens* (silhouettes), respectively.

References

1. S. N. Fernandes, P. L. Almeida, N. Monge, L. E. Aguirre, D. Reis, C. L. P. de Oliveira, A. M. F. Neto, P. Pieranski, and M. H. Godinho, Adv. Mat., **29**, 2, 1603560 (2017).

Cholesteric self-assembly of a cellulose nanocrystal suspension in a shrinking microdroplet

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Cellulose Nanocrystals (CNCs) are biosourced, colloidally stable elongated nanorods that form chiral nematic liquid crystals above a threshold concentration. Their cholesteric order can be retained upon drying to form chiral nanostructures that can display structural color. Inspired by the helicoidal architectures found in the plant cell wall,[1] we report the self-assembly of cellulose nanocrystals (CNC) into hierarchical cholesteric architectures within micron-sized aqueous droplets.[2] This confined, spherical geometry drastically affects the colloidal self-assembly process, resulting in concentric ordering within the droplet, as confirmed by simulation. This provides a quantitative tool to study in situ the pitch evolution upon concentration increase beyond what has been achieved in a planar geometry. This methodology allows us to fabricate truly hierarchical solid-state architectures, from the nanometre to the macroscopic scale using a renewable and sustainable bio-polymer.



Figure. (A) Polarization optical micrograph of the generation of microfluidic droplets containing cellulose nanocrystals (CNC). (B) Comparison between the theoretical (left) and experimental (right) assembly of the cholesteric CNC suspension within a microdroplet. (C) SEM images of a dry CNC microparticle (top), showing the helicoidal assembly of CNC within the particle (bottom).

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Chiral assemblies along cellulose nanocrystals

Olli Ikkala

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Cellulose nanocrystals (CNC) have already long recognized to allow left--handed cholesteric liquid cystallinity due to the slight right--handed chiral twisting along the individual CNC rods. To directly visualize the latter, we applied high resolution transmission electron tomography [1]. Challenges were encountered due to the required resolution. To promote radiation tolerance, the individualized CNCs were next ionically complexed with cationized Au--nanoparticles [2]. This lead lateral aggregation of a few CNCs, right--handed CD--signal, and chiral plasmonics. Towards next templating tunable helical structures, CNCs were first decorated with anionic polymer brushes, and complexed with double hydrophilic diblock copolymer with a cationic block undergoing interpolyelectrolytic complexation with the anionic brush. Depending on the polymer lengths, CNCs with helically twisting surface topographies were observed [3].



Figure. a) Right handed chiral plasmonics using CNCs with ionically complexed cationic Au nanoparticles, b) Helically twisting surface structures along CNCs upon ionic complexation of diblock copolymer on oppositely charged surface brushes around CNCs.

- J. Majoinen, J. Haataja, D. Appelhans, A. Lederer, A. Olszewska, J. Seitsonen, V. Aseyev, E. Kontturi, H. Rosilo, M. Österberg, N. Houbenov, O. Ikkala, J. Am. Chem. Soc., 136(3), pp. 866–869 (2014).
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Magnetic Alignment of Cellulose Nanocrystals in Suspension and in Hydrogels: Kinetics and Order Parameters

Kevin De France, ¹ Todd Hoare, ¹ Kevin G. Yager² and <u>Emily D. Cranston</u>¹ ¹Department of Chemical Engineering, McMaster University, 1280 Main St. West, Hamilton, ON, Canada ²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, USA

Cellulose nanocrystals (CNCs) align in suspension when subjected to external forces, such as electric/magnetic fields and shear stress. The ability to orient CNCs is significant for a number of applications including the production of composite materials with enhanced mechanical performance, control of CNC optical properties in liquid and dried states, as model surfaces to study cellulose interactions, and as templates and scaffolds such as those used in tissue engineering. Above a critical concentration in suspension, CNCs self-assemble into a chiral nematic liquid crystal phase and it has been well documented that CNCs align perpendicular to a magnetic field. However, the cooperative nature of this assembly, the effect of magnetic field strength and the associated alignment kinetics have been largely uninvestigated.

This presentation will describe the use of small angle x-ray scattering (SAXS) to capture the real time ordering of CNCs in relatively weak magnetic fields (up to 1.2 T) in both aqueous suspension and in an injectable PEG-based hydrogel. This is the first experimental evidence of significant CNC alignment achieved in such a low magnetic field over short time periods. For CNC suspensions above the critical concentration, the time evolution of alignment was well described by a sigmoidal equation (i.e., cooperative ordering) with initial ordering related to the magnetic field strength. After 129 minutes at 1.2 T, nearly perfect anti-alignment (S=-0.499) of CNCs was achieved and a uniform chiral nematic texture across the entire sample was observed.[1] In the injectable hydrogel matrix, the CNC concentration was orders of magnitude below the critical concentration but magnetic alignment was observed nonetheless. An order parameter of only S=-0.1 was achieved (almost instantly) and was "locked" into the quickly gelling system.[2] This demonstrates that alignment of very low concentrations of CNCs can be obtained if the surrounding media does not allow for fast relaxation, and indicates that the formation of magnetically ordered CNC materials is more readily accessible than previously thought.



Figure. Experimental SAXS setup and evolution of order parameter over time showing cooperative ordering of a CNC chiral nematic suspension.

References

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Phase Behavior, Rheology, and Solidified Microstructure of Aqueous Cholesterogenic Nanomesogen Systems

Partha Saha¹, Matthew Noor¹, Martin Pospisil,² Micah J. Green,² <u>Virginia A. Davis</u>¹ ¹Auburn University, Department of Chemical Engineering, Auburn University, AL, USA ²Texas A&M University, Department of Chemical Engineering, College Station, TX, USA

Controlling the final microstructure and properties of solid materials (e.g. coatings, films, fibers) assembled from lyotropic nanomesogens requires understanding their phase behavior, quiescent microstructure, rheological behavior and the microstructural changes that occur during solvent evaporation. This research compares the properties of cholesterogenic aqueous dispersions of sulfonated cellulose nanocrystals (CNC)^{1,2} and single walled carbon nanotubes (SWNT) stabilized by double-stranded DNA (dsDNA).^{3,4} These two systems differ significantly in terms of the relative importance of electrostatic and van der Waals forces, mesogen aspect ratio, and mesogen rigidities. A key distinction between the two systems is that the high ionic strength of the CNC system results in the viscosity versus concentration curve not exhibiting a minimum at the biphasic to liquid crystal transition. In contrast, the dsDNA/SWNT system does exhibit this minimum which is typically associated with the biphasic to liquid crystal transition for macromolecular lyotropic dispersion. This rheological behavior directly affects the processing of the dispersions into films.



Figure. Viscosity versus concenetration for A.) aqueous sulfonated CNC and B.) dsDNA/SWNT. Closed symbols indicate steady shear, open symbols indicate oscillatory shear.^{1,4}

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- 2. Haywood, A. D.; Davis, V. A. Cellulose, 24, 705 (2017).
- 3. Ao, G.; Nepal, D.; Aono, M.; Davis, V. A. ACS Nano, 5, 1450 (2011).
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Session 2:

Theory and simulations of cholesteric phases

Spontaneous formation of chiral systems from achiral liquidcrystalline molecules

<u>Mark R. Wilson</u>, Martin Walker Department of Chemistry, Durham University, Lower Mountjoy, Durham, DH1 3LE, UK *E-mail: Mark.Wilson@durham.ac.uk*

Chirality arising from achiral molecules occurs in many liquid crystal systems. We show results from two simulation studies in which this phenomenon occurs.

1) In a DPD model of a disc-shaped chromonic molecule, containing a combination of hydrophilic and hydrophobic-lipophobic chains, self-assembly in water leads to the formation of novel complex aggregates with a three-molecule cross-section. These aggregates display a spontaneous twist to produce chiral structures (see figure), together with dynamic chirality inversion [1,2].

2) When certain achiral bent core mesogens are added to a chiral nematic liquid crystal, the chirality is seen to increase, contrary to expected behaviour [3]. We show that molecular conformations exist, which have extremely high helical twisting powers, orders of magnitude higher than those seen in conventional chiral dopants. We provide a simple simulation model that demonstrates both preferential selection of chiral conformations and chirality transfer between solvent and solute, leading to an increase in the helical twist of a chiral nematic phase.



Figure. Dynamic chirality inversion in a chromonic stack formed from achiral chromonic amphiphiles.

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- 2. M. Walker, A. J. Masters, M. R. Wilson, Phys. Chem. Chem. Phys., 16, 23074-23081 (2014).
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Is chirality always needed to obtain twisted molecular organizations?

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Twisted molecular organizations are typically originated by chiral constituent particles, like in cholesteric or smectic C* liquid crystals obtained from chiral mesogens or by seeding an achiral phase with chiral dopants [1]. On the other hand, similar structures can be obtained in sufficiently thin films by the effect of suitable external boundaries, like in Twisted Nematic displays[2], or by a chiral surface inducing twist in a nematic. The situation is much less obvious if the confining surfaces are just those of a hybrid film [3] or even not present, like in a isolated nematic nanodroplet that can become chiral [4, 5]. Computer simulations are currently very useful for examining the relation between molecular and overall chirality, both for simple rigid molecules [5] and for realistic atomistic simulations [3]. However, a problem that has to be solved, and that is often neglected in published literature, is that of assessing and objectively quantifying the instantaneous and average chirality, both of the constituent molecules, particularly when they have conformational freedom [6, 7] and, even more importantly, of the resulting self-assembled structures. In the talk we discuss various examples of chirality assessment from the computer simulation of various model Gay-Berne based systems [2, 5] and realistic systems like chiral islands of sexithiophen [8] and odd cyanobiphenyl dimers [9] that are experimentally found to form heliconical phases [10].

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Twist-Bend Phases in mixtures of chiral and achiral molecules

Akihiko Matsuyama

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We present a mean field theory to describe phase transitions in binary mixtures of a chiral and an achiral liquid crystalline molecule in the presence of an external field. When a longitudinal external field is applied parallel to the pitch axis of the cholesteric (C_h) phase, the director of the C_h phase can lead to a twist-bend distortion [1,2], due to the coupling between the external field and the director. We predict that a twist-bend distortion, or a twist-bend cholesteric (C_{TB}) phase, exists between C_h and nematic (N) phases on the temperature-concentration plane. We find various phase transitions: the first-order C_{TB} -I(isotropic) and the second-order C_{TB} -N, C_{TB} -C_h phase transitions. We also predict the phase diagrams, depending on temperature, concentration and the external field.

Figure 1 shows the phase diagram on the temperature T/T_{NI} and the external field h plane for the volume fraction ϕ_A of the chiral molecules: $\phi_A=0(black)$, $\phi_A=0.1$ (red) and $\phi_A=0.5$ (blue). The solid curves show the second-order phase transitions: N-C_{TB} and C_{TB}-C_h transitions. The dotted-curves show the first-order phase transitions: I-N, I-C_{TB}, and I-C_h transitions. The closed circles show the critical point (CP).



Figure. Phase diagram on the temperature T and external field h plane for various concentrations of chiral molecules.

- 1. A. Matsuyama, Liq. Cryst. 43, 783-795 (2016).
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Percolation of Hard Rods in the Uniaxial Nematic Phase

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In geometric percolation, two hard particles are connected if their shortest surface-to-surface distance is smaller than some cut-off distance known as the connectedness criterion.¹Clusters are then defined as collections of mutually connected particles. In a dispersion, the average number of particles in a clusterincreases with increasing particle loading and diverges upon approach of the percolation threshold. The network of connected particles becomes system-spanning at the percolation threshold, and the physical properties of the dispersion change drastically beyond it. This is why the percolation threshold is an experimental observable.

For fluid dispersions of long rod-like particles, such as carbon nanotubes, the percolation threshold must depend on whether the particles are in the isotropic or in the uniaxial nematic phase, which for long rods appears at very low packing fractions. Theory and simulations have so far focused entirely on percolation in the isotropic phase. It is well-established now that for realistic connectedness criteria, percolation occurs near the isotropic-nematic phase transition,^{2,3} and that alignment of the particles by external fields may shift or even suppresses it.^{2,4}

We study percolation in the nematic phase of hard spherocylinders by means of Monte Carlo simulation and connectedness percolation theory. We find that there is a range of values of the connectedness criterion for which percolation does occur in the nematic phase, even under conditions where it does not occur in the isotropic phase. If the connectedness criterion drops below a critical value, then the percolation threshold shifts to concentrations in excess of that where the isotropic-to-nematic transition takes place.

We find that clusters of rod-like particles in the nematic phase are highly anisotropic, that is, they are very much longer along the director field than perpendicular to that. Still, upon approach of the percolation threshold both the length and the width of the clusters diverge with the same critical exponent. The fractal dimension of the clusters in the nematic phase remains two, the same value as of clusters in the isotropic phase, owing to the mean-field character of the theory. The potential impact of twisted (cholesteric) order will be discussed.

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Density-functional theory for cholesteric phases of realistic flexible particles

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Lyotropic cholesteric phases are commonly observed in many bio-colloidal and polymer solutions, characterised by a complex interplay between thermal fluctuations, entropic and molecular forces. The difficulty of achieving accurate microscopic descriptions of these many competing factors has led to the introduction of strongly coarse-grained theoretical models, whose microscopic underpinnings are highly nontrivial [1]. Furthermore, the wide lengthscale discrepancy between typical particle sizes and experimental pitches has largely thwarted direct numerical investigations of cholesteric self-assembly for all but the simplest model systems [2].

We here introduce a comprehensive numerical framework based on density functional theory [3] to investigate the cholesteric behaviour of generic particles in the weak chirality limit. This approach, built upon the use of highly-efficient Monte-Carlo methods for the computation of virial-type integrals, enables us to tackle arbitrarily complex mesogen models and interaction potentials. We illustrate its application to systems of near-persistence-length DNA duplexes as described by a well-documented molecular model coarse-grained at the nucleotide level [4] (Fig. 1), and investigate the relative roles of excluded volume, electrostatics and particle flexibility on phase behaviour and cholesteric pitch. We finally consider potential shortcomings of the theory in terms of symmetry assumptions and inter- article correlations, and discuss prospective directions for future improvements.



Figure. Model system of 146 base-pairs DNA duplexes

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Hierarchical propagaton of chirality through reversible polymerizaton: the cholesteric phase of DNA oligomers

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Although chiral nematic ordering has been repeatedly observed and studied in various lyotropic systems [1], a quantitative account for the macroscopic chirality on the basis of the chiral structure of its microscopic constituents represents a challenge for theory and computations. Here, we consider the chirality of the nematic ordering that develops in solutions of palindromic DNA dodecamers via their selfassembling into weakly bound linear chains. In this system the cholesteric pitch has a non-trivial dependence on both DNA concentration and temperature. In order to grasp a physical understanding of this complex behavior, we developed a novel theoretical approach that bridges the structure and chirality of the elementary building blocks to the helical organizaton of the self-assembly-driven cholesteric phases. Our theoretical approach combines an Onsager-like theory for orientational order, extended to the elastic and chiral properties of the cholesteric phase, with a theory for self-assembly-driven nematic liquid crystals [2]. Noticeably, our theory contains no adjustable parameters other than those previously determined from the phase behavior. We also performed new accurate experimental measurements of the cholesteric pitch, as a function of temperature in samples at different concentrations. In these samples a right-handed cholesteric phase is formed, with a pitch of few microns, which increases with lowering temperature and increasing concentration. The good quantitative agreement (see Figure) between theoretical and experimental results allows us to unveil the physical mechanisms at play in the propagaton of chirality and to identify in the



temperature and concentration dependence of the pitch an hallmark of self-assembly.

Figure. Comparison of experimental and theoretical pitch for liquid crystal cholesteric solutons of Dickerson dodecamer. (a) Pitch as a function of temperature along isochores, from experiment (symbols) and theory (lines). Concentrations (mg/ml) are given in the legend. (b) and (c) show cholesteric textures for two different state points.

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Session 3:

Chiral nanorod suspensions: from particle tuning to self-assembly

Twisted Cellulose

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Lignocellulosic materials often display twisted structures at many length scales. Tree trunks, wood sections, paper strips, wood cell walls, cellulose microfibrils, nanocellulosic materials and cellulose derivatives all display a spontaneous twist under appropriate conditions. In many cases, the twist is chiral, displaying a single handedness. The cellulose molecular structure of natural polysaccharides such as cellulose is also chiral, but the relationship between molecular chirality and higher expressions of chirality in natural materials is poorly understood. The twisted organization of chiral nematic phases in suspensions of cellulose nanocrystal (CNC) suspensions [1] should provide a tractable in vitro system linking molecular and macroscopic chiral structures. Difficulties remain. Most theoreticians now agree that crystalline natural cellulose should form nanofibrils with a right-handed helical twist, but experimentalists have difficulty providing solid evidence for this twist in nanocellulose samples from cotton or wood pulp. Conversely, experimentalists have strong evidence that suspensions of CNC normally form a lefthanded helicoidal arrangement in suspension, but theoreticians have a hard time explaining why. It is also clear that the twisting inherent in chiral nematic phase formation is in competition with the tendency of concentrated solutions and suspensions to undergo kinetic arrest due to gelation and glass formation [2, 3]. While many questions remain, there has been significant recent progress in understanding the ordering and twisting tendency of chiral natural materials.

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Kinetic Control of Chiral Self Assembly

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We invstigate the aggregation process for a group of related six-residue peptides forming amyloid fibrils and amyloid-like microcrystals. We observe experimentally the production of chiral assemblies having either right, left or no handedness at the morphological level based on control of the sequence and of the solution conditions. Using theory, and also atomistic and higher-level modelling, we motivate the mechanisms for kinetic selection of the different selfassembly pathways.

Compensated cholesterics of helical mesogens: insights from simple microscopic models

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We study the pitch of cholesteric assemblies of helicoidal patchy cylinders as a generic model for chiral biopolymers and helix-shaped colloids. Using microscopic theory and computer simulation we find that the handedness of the chiral assembly may spontaneously flip sign upon changing the system density or temperature while preserving the chiral features of the individual particles. We show that these inversions are generic and can be expected in cholesteric phases of both thermotropic and lyotropic origin [1,2]. The mechanism underpinning the symmetry inversions can be explained in terms of an antagonistic effective torque acting between helical rods. In a second model we take a closer look at steric chirality of weakly curled hard rods in order to assess the impact of short- versus long-ranged chiral forces on the pitch [3]. In the final part I will briefly discuss the role of director fluctuations and the impact of concentration fluctuations and external fields on the topology of the helicoidal director field.

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Rigid filaments with varying chirality and tunable shape

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Polymeric suspensions are traditionally classified into three categories depending on the rigidity of the filament backbone: flexible coils, semi-flexible filaments and rigid rods. Using bacterial flagella as the basic building block we describe a model system of rigid chiral filaments with two unique features. First, the flagella-based filaments are not rodlike but have a spatially varying curvature. Second, in response to applied external stimuli these filaments undergo large-scale polymorphic shape changes. We study properties of dense isotropic suspensions of such filaments. Using optical microscopy, we quantify how the shape of the constituent rigid filaments affects the microscopic dynamics and relate this information to macroscopic rheological properties. Certain filaments shapes are permanently jammed at extremely low volume fractions and effective behave as cross-linked gels. Finally, we describe preliminary results in which we switch filament rheology by inducing shape changes of the constituent filaments.

Rod-like Viruses as Model System for Studying Chirality Amplification in Colloidal Liquid Crystals

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Rod-like viruses with their features like monodispersity and their ability to organize in ordered structures motivate the strong interest they have raised as model systems for soft condensed matter. Suspensions of rod-like viruses form a variety of liquid crystalline phases [1], whose general behavior can be explained in terms of a few parameters, namely the volume fraction and the rod aspect ratio [2].



Figure. Filamentous virus observed by electron microscopy with a schematic representation of its capsid, and polarizing optical microscopy picture of the cholesteric phase formed by virus suspensions (Image size: 750µmx500µm).

In this context, filamentous viruses and their mutants represent a paradigm for studying the connection between chirality of the elementary building blocks and the macroscopic twist displayed by the liquid crystalline phases [3,4,5]. If some investigation has been already done to predict the cholesteric twist (pitch and handedness) based on the microscopic features of the viral particles [6], we will present here recent results on chemically and biologically modified viruses [7], where the balance between the different chiral contributions (steric, electrostatic, excluded-volume...) of opposite handedness will be discussed.

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Twist and shout: chirality amplification and fluctuation modes in the cholesteric phase of short DNA

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Predicting how the molecular chirality propagates up to the mesoscale remains a challenge even for systems in which the molecule has the simple form of a straight helix. This is the case of DNA short double strands, whose concentrated aqueous solutions show Cholesteric (N*) liquid crystalline (LC) ordering, mediated by the reversible end-to-end aggregation of duplexes into linear aggregates. Right-handed DNA helices show an extremely diverse behaviour, with both left- and right-handed N* phases and pitches from the visible range up to several μ m [1]. The N* behaviour depends on the length and sequence of the oligomers, and on their aggregation mode [2]. The combination of these parameters determines the concentration range of the N* phase, setting the balance between electrostatic and steric interactions and thus phase handedness.

Measuring viscoelastic properties of N* can provide important information on chiral torque and the delicate interplay of underlying molecular interactions. However, traditional light scattering techniques cannot be used in samples like DNA because of the lack of suitable alignment strategies. To study thermal fluctuation of N* textures, we thus exploit the unique space-resolving capabilities of polarized Differential Dynamic Microscopy (p-DDM), recently demonstrated for Nematic LCs [3].

Here, we extend p-DDM to the more complex, coupled N* modes [4], and validate it with a thermotropic LC, finding good agreement with literature data. Similar measurements performed on DNA N* enable extracting splay-bend and twist viscoelastic constants as a function of temperature. Surprisingly, we also find an additional mode with non-diffusive relaxation, possibly related to the end-to-end aggregation.



Figure. Short DNA helices self-assemble and order into Cholesteric phase, whose viscoelastic ratios can be extracted from Fourier analysis of fluctuations in microscopic textures.

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Session 4:

The route to applications

Cellulose photonics: from nature to applications

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Nature's most vivid colours rely on the ability to produce complex and hierarchical photonic structures with lattice constants on the order of the wavelength of visible radiation [1]. A recurring strategy design that is found both in the animal and plant kingdoms for producing such effects is the helicoidal multilayers [2]. In such structures, a series of individual nano-fibers (made of natural polymers as cellulose and chitin) are arranged parallel to each other in stacked planes. When distance between such planes is comparable to the wavelength of light, a strong polarised, colour selective response can be obtained. These helicoidal multilayers are generally structured on the micro-scale and macroscopic scale giving rise to complex hierarchical structures.

Biomimetic with cellulose-based architectures enables us to fabricate novel photonic structures using low cost materials in ambient conditions [3,4]. Importantly, it also allows us to understand the biological processes at work during the growth of these structures in plants. In this talk the route for the fabrication of complex bio-mimetic cellulose-based photonic structures will be presented and the optical properties of artificial structures will be analysed and compared with the natural ones.



Figure. Picture of *Margaritaria nobilis* fruits, the intense blue coloration is the results of the helicoidal architecture of cellulose in the cell wall in the epidermis of the fruits.

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Single-Fibril Properties and Assembly of Nanocellulose-Based Hybrid Materials

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Optimal design of hybrid materials requires integration of appropriate and efficient approaches to synthesize, functionalize, characterize and process the nanosized species for specific applications. Here, I will give an overview of recent research on characterization and surface modification of nanocellulose fibrils [1] and the fabrication of nanocellulose-based hybrid films and super-insulating foams.

We have studied the structural features on multiple length scales of rod-like cellulose nanoparticles by applying statistical polymer physics concepts and assessed their physical properties *via* quantitative nanomechanical mapping [2]. We show clear evidence of a righthanded chirality and statistical analysis of tracked contours shows that the kink angle distribution is inconsistent with a CNF structure consisting of alternating amorphous and crystalline domains. I will demonstrate how the microstructure and mechanical, and thermal properties of various inorganic-nanocellulose hybrids can be tailored by controlling the foaming and assembly of nanocellulose and the inorganic nanoparticles. Examples include nacre-like hybrids based on nanocellulose and calcium carbonate [3], and hybrids of cellulose nanofibrils and titania nanoparticles that results in transparent and flexible free-standing films with a hardness comparable to concrete. Freeze- asting suspensions of cellulose nanofibres, graphene oxide and sepiolite nanorods can produce super-insulating, fire-retardant and strong anisotropic foams. The sepiolite and graphene oxide contribute together with the cross-linker boric acid to the excellent combustion resistance, being significantly better than traditional polymer-based insulating materials [4].

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Engineering of Chiral Phases from Cellulose Nanocrystals: Effect of CNCs Dimension and SO₃ content

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One-dimensional rod-like nanostructures with high aspect ratio (10-50) and chiral surface centers such as cellulose nanocrystals (CNCs) are popular light-weight natural nanomaterials with intriguing properties, such as extraordinary mechanical performance, optical transparency and anisotropy, low thermal expansion, low density, large specific surface area, biodegradability and availability [1,2]. Furthermore, the anisotropic shape of these cigar-like nanocrystal (100-500 nm length and 3-20 nm in diameter) provides opportunities to create stimuli-responsive chiral phases at high concentrations (Fig. 1). Despite a number of recent examples on chiral nematic organization, strong chiral laminated nanocomposites, or tunable photonic crystals, some fundamental questions important for the development of novel lightweight mesophase CNC materials with unique mechanical, tunable photonic properties are still not addressed. Among critical issues to be considered are the precise control of CNCs dimension and SO3 content at the CNCs surface in order to balance local packing and tuning of structure of chiral phase. Here we demonstrate that the size and aspect ratio of CNCs are dependent on the cellulose source. The sources based wood pulp lead to longer nanocrystals with hight aspect ratio. At the same time, sources based microcrystalline cellulose form shoter CNCs with lower aspect ratio. Thus, by selecting different CNC sources, we demonstrate that aspect ratio is an effective parameter to engineering CNC based mesophases in dry and liquid state. Namely, CNCs with a smaller aspect ratio form chiral phases with a smaller pitch value. Removing of solvent from the LC chiral phases decreases the absolute value of pitch, but the trend between aspect ratio and pitch is preserved allowing for simple tuning of structure and photonic properties of CNCs based chiral phases.Figure. AFM image of CNCs (a) and their chiral phase (b).

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Organized thin films of cellulose nanocrystals: From model to optically active films

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Organized thin films of cellulose nanomaterials have attracted a great interest for their spectacular optical properties but also because they can be used as model to elucidate the nature of the interactions in fiber cell walls and composites among other applications. Since few years many dedicated efforts have been directed toward the manufacturing of highly organized and robust nanofilms based either on pure nanocellulose substrates or in blend with other polymers. Different techniques such spin coating, barre coating, Langmuir-Blodgett, Langmuir-Scheafer, Spray-assisted deposition and shear convective deposition were used for the manufacturing of such organized films leading to nanomaterials with tunable properties useful for wide range of fundamental and applied domains. This presentation will provide an overview of these efforts and highlight some important findings.

Dynamically controlled iridescence of cellulose nanocrystal assemblies with electric field

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Natural structures are often made of hierarchically organized assemblies of nanometric elements, with precise functions, like the helicoids in the iridescent beetle shells. Cellulose nanocrystals (CNCs), isolated e.g. by sulphuric acid hydrolysis from cellulosic fibers, are one of the typical model of chiral nanorods with dimensions of 2-50 nm in diameter for up to several microns in length depending on their biological origin [1]. When dispersed in apolar solvents using surfactants, CNCs spontaneously phase-separate into chiral nematic structures, but at much higher concentrations than in those already observed in aqueous media. The chiral pitch decreases to a few microns, revealing a stronger chiral interaction [2] and beautiful iridescent colors in suspension.

Additionally, CNCs can be oriented by relatively modest electric fields [3]. Recently, we also showed that these colloids bear a permanent dipole as high as 4000 Debye [4]. Combining this orientation features with the self-organization properties, we showed that it is not only possible to orient the cholesteric domains, but also to unwind the cholesteric axis to any desired pitch value as shown by laser light diffraction and iridescence. These spectacular features allow the controlled production of iridescent substrate with tailored properties, and even a dynamical control of the orientation.



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Flexible Chiral Nematic Cellulose Nanocrystals Film with Brilliant and Tunable Structural Color

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Cellulose nanocrystals (CNCs), which have also been named as cellulose nanowhiskers or nanocrystalline cellulose, are rod-like or whisker shaped particles with diameters of a few nanometers and a screw symmetry. The physical principles behind structural colors have inspired numerous efforts to generate photonic materials based on cellulose nanocrystals. In the colorful biological world, the animals that use camouflage such as *Paracheirodon innesi*, *Charidotella egregia* can reversibly change their structural colors in response to external stimuli in the surrounding environment [1]. Inspired from these animals, we have developed flexible and chiral nematic CNC/polyethylene glycol (PEG) composite films that exhibit humidity-responsive structural color change (Figure 1).



Figure. a) Water uptake of the CNC and CNC/PEG composite films. b) UV-Vis spectra of the CNC80PEG20
 composite film at different relative humidity (RH). c) Photographs of the CNC80PEG20 composite film at different RH. d) Reversible conversion of the stopband position of the CNC80PEG20 composite film by exposing to increasing and decreasing RH conditions between 30% and 100%.

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Posters

P₁

3D finite-element simulations of cellulose nanocrystal alignment dynamics

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In order to study the formation of chiral structures in cellulose nanocrystal (CNC) suspensions, we develop a 3D finite element model that incorporates the Landau-de-Gennes equation for the orientation dynamics of chiral nematics. This model allows a clear comparison of chiral strength, short range intermolecular interactions, and long-range Frank elasticity. In conjunction with the experimental results of Davis et al., our system focuses on structural dynamics after the cessation of flow where the system relaxes from an aligned state and forms chiral structures. Specifically, we compare optical microscopy images against simulation results (and simulated micrographs) as chiral structures are formed, and we compare pitch values as a function of composition. (Pitch is computed using spatial Fast Fourier analysis.)



$\mathbf{P}_{\mathbf{2}}$

Cellulose nanocrystal films' new photonic properties

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Cellulose nanocrystals' (CNCs) solid films present remarkable optical properties as iridescence, as well as selective light reflection derived from its cholesteric organization. [1] Within its structure one can find different cholesteric domains [1], that reflect different colours, and also some micrometer-gaps [2]. If these micro-scale planar gaps, observed perpendicular to the CNCs films' cross-section between two different lefthanded films' cholesteric domains, are impregnated with a nematic liquid crystal (LC), a new photonic structure is produced (Figure 1). The LC layer acts as a half-wave retardation plate and the new composite system of CNC iridescent film/nematic LC reflects both right circularly polarized (RCP) and left circularly polarized (LCP) light [3] as observed in certain beetles cuticula, ex. the Plusiotis resplendens [4]. This CNC's new photonic structure is reversibly tuned by the application of, for instance, an electric field or a temperature variation. The same phenomenon was observed for devices derived from cellulose nanocrystals/biocompatible polymer composite films filled with a LC.



Figure. a) Cross-section image of a microgap present in a CNC/polymer composite film; Photographs of composite system observed with white light b), and circularly polarized light (c-d).

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The chiral nematic phases formed by hard helices

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We have investigated the phase diagram of hard helical particles using an Onsager--like theory and Monte Carlo simulations and we have found a rich polymorfism, which includes two different nematic phases with helical order. One is the *cholesteric*, where the director, i.e. the average alignment direction of particles, rotates around a perpendicular axis with a perodicity that is orders of magnitude longer than the helical pitch of the particles [2]. In the other chiral nematic phase, that we have denoted as *screw*, it is the two--fold symmetry axis of particles that spirals around the director, with periodicity equal to the particle pitch [3]. Several examples of the cholesteric phase can be found in natural and synthetic systems (see [4,5] for recent reviews); the only requirement for its formation is that the microscopic constituents are chiral. On the contrary, the screw--nematic phase requires that its constituents have a helical shape and, to our knowledge, the only experimental evidence of this phase is in suspensions of helical flagella [6]. Here we will discuss the origin of the two different chiral nematic phases and we will illustrate the relationship between the features (pitch and handedness) of these phases and the morphology of the constituent helical particles.

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\mathbf{P}_4

Influence of structural properties of cellulose nanocrystals on the formation of the liquid crystalline phase

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The increasing interest in alternative materials to fossil fuels has been the driving force for many research efforts towards biodegradable, renewable materials. Particular attention is paid to cellulose, partially because it is the most versatile and abundant biopolymer in nature, but even more because of the possibility to isolate and utilize novel forms of cellulose that have at least one dimension in the nanometer range.[1] Full utilization of the intrinsic properties of the stiff, rodlike cellulose nanocrystals, which form a chiral nematic liquid crystalline phase with interesting optical behaviour, requires a better understanding of their properties and behaviour for controlling their assembly over several length scales.[2]

We have studied the packing of different aspect ratio CNCs obtained from wood [3] and cotton sources in the chiral nematic phase. The inherent structural properties have been investigated by small angle X-ray scattering and their influence on the formation of the liquid crystalline phase will be discussed.

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P₅

Fractionation of cellulose nanocrystals

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Cellulose nanocrystals (CNCs), nanorods produced by acid hydrolysis of cellulosic sources, are emerging as a new class of functional biomaterial. CNCs present a broad range of uses, for example in composites, cosmetics, security paper and medical devices [1]. The fascinating ability of CNCs to self-organize into a cholesteric liquid crystal phase, with a helical arrangement of the nanorods, is attracting substantial interest across different research fields [2].

A critical problem from an analytical, and likely also from an applied perspective, is the high length polydispersity of as-produced CNC samples. In this study, we introduce a method for fractionating the CNC nanorods, utilizing the spontaneous phase separation between isotropic and liquid crystalline phases, allowing us to shift the length distribution diagram. The aspect ratio has a strong effect on the period of the cholesteric helix and the volume fraction. We present how this affects the self-assembly process, and consequently the color formation in such bio-derived structural films.

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P₆

Simulations of helical Yukawa rods as a model for cholesteric liquid crystals

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Cholesteric liquid crystals show a rich phase diagram, including the usual isotropic, nematic and smectic phases, and the special cholesteric (chiral nematic) phase. Especially biological materials show this cholesteric phase, e.g. *fd* viruses and cellulose nanocrystals [1].

Our aim is to explore the complex phase diagram of helical Yukawa rods, which are an example of simple model chiral mesogenes, by Monte Carlo simulations. The rods are hard spherocylinders with a helical distribution of discrete charges on their surface, which interact via a Yukawa (screened Coulomb) potential. A similar model has already been studied analytically by Wensink and Jackson [2]. Of special interest is the simulation of equilibrium cholesteric pitches. For this, we introduced a new method including soft walls and self- determined boundary conditions [3].

We study the dependence of the maximum density after isobaric compression of an isotropic system on a number of parameters: surface charge, added salt concentration and internal pitch of the charge helix. By decreasing the internal pitch, the local alignment of rods is reduced, resulting in a lower maximum density. The internal pitch also determines the strength of twist in (pancake-like) membranes of helical Yukawa rods.

The influence of aspect ratio on the isotropic-cholesteric transition and the cholesteric pitch is another part of our investigation.

Figure. Left: Sketch of helical Yukawa rods used as model for cholesteric liquid crystals with length L, diameter D and internal pitch p^{int} . Right: p^{int} Cholesteric phase of the model system (color shows orientation).

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P₇

Biaxial shapes and nematic liq1uid crystal phases: towards twist-bend nematics

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We investigate the infl uence of the shape of hard biaxial particles on the formation of prolate, oblate, and biaxial nematic liquid crystal phases. The biaxiality and polarity of the phase and the particles is included through a general formulation of Onsager-Parsons-Lee theory. For a given particle shape, the angular dependence of the excluded volume is expanded in Wigner matrices and the corresponding coeffcients are calculated using Monte Carlo. We construct phase diagrams for different types of hard biaxial particles, including bricks and boomerangs, as a function of packing fraction and particle anisometry. The resulting phase diagram for boomerangs is shown in the figure. In addition, we show that this general framework can be readily extended to include the spatial modulation of the nematic director in a chiral or twistbend nematic phase.



Figure. Phase diagram for boomerang particles with equal length arms $(L_1 = L_2 = 10D)$ as a function of the angle χ and the packing fraction η . At low packing fraction, an isotropic phase (I) is found, while at higher packing fractions oblate (N₋), prolate (N₊), and biaxial (B) nematic phases are found, with two Landau points at approximately $\chi = 52:5$ and $\chi = 105$.

P_8

Beyond Buckling: Humidity-Independent Measurement of the Mechanical Properties of Cellulose Nanocrystal Films

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Precise knowledge of the mechanical properties of nanomaterials and nanocomposites is crucial to match their performance with suitable applications. While methods to characterize mechanical properties exist, they are limited by instrument sensitivity, sample requirements and, in the case of bio-based nanomaterials, extreme humidity dependence. We present a new approach, based on buckling mechanics, to determine the elastic modulus of cellulose nanocrystal (CNC) thin film composites or aligned CNC films, in a humidity-independent manner. Composite films were prepared using layer-by-layer (LbL) assembly with CNCs and water-soluble polymers on prestressed polystyrene substrates. Aligned CNC films were solvent cast on pre-stressed polystyrene substrates which had been plasma treated to change the wettability. Chiral nematic, radial alignment and parabolic focal conic defect textures were reproducibly achieved depending on the drying parameters. Films on the pre-stressed polystyrene were shrunk by heating above the polymer glass transition temperature. The compression during shrinking led to wrinkled films with hierarchical structures and characteristic topographies. Films were found to have humidityindependent elastic moduli (calculated from FFT analysis of SEM images) that varied with the composition and degree of CNC alignment. This structuring method is straightforward and amenable to a wide range of supported thin films, and fills an existing gap in the available methods to measure nanomaterial mechanical properties.



Figure. (Left) Parabolic focal conic defect texture of a CNC film on pre-strained PS substrates imaged by polarized optical microscopy; and (right) CNC films after shrinking, imaged by SEM, size: 10 µm across.

Liquid Nanocrystalline Cellulose Aqueous Suspensions: Rheological Effects

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The rheological properties and microstructure of nanocrystalline cellulose (NCC) aqueous suspensions have been investigated at different concentrations. The suspension is isotropic up to 3 wt.%, and phase separates to liquid crystalline and isotropic domains at higher concentrations where the samples exhibit a fingerprint texture and the viscosity profile shows a three-region behavior, typical of liquid crystals. The suspension behaves as rheological gel at even higher concentrations where the viscosity profile shows a single shear thinning behavior over the whole range of shear rates investigated [1,2]. The effects of ultrasound energy and temperature on the rheological properties and structure of these suspensions were studied using polarized optical microscopy and rheometry [1]. Our results indicate that the amount of applied ultrasound energy affects the microstructure of the suspensions, and the pitch of the chiral nematic domains. The viscosity profile is changed significantly at low shear rates, whereas the viscosity of biphasic suspensions at intermediate and high shear rates decreased with increasing temperature. This suggests that between 30 and 40 °C, structural rearrangement takes place. At higher concentrations of about 10 wt.%, the temperature has no significant effect on viscosity, however, a marked increase in viscosity has been observed at around 50 °C. Finally, the Cox-Merz rule was found to fail after a critical concentration, thereby implying significant structural formation. This critical concentration is much higher for sonicated compared to unsonicated suspensions.

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P₁₀

Influence of the Particle Concentration and Marangoni Flow on the Formation of Cellulose Nanocrystal Films

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Cellulose nanocrystals, rod-like crystalline nanoparticles, are a bio-based material that can be a great alternative to obtain films with tunable optical properties. Iridescent and light diffracting films can readily be obtained via the drying of a suspension of these cellulose nanocrystals. The characteristics of the particle deposition process together with the self-assembly in the precluding suspension has a direct effect on the optical properties of the obtained films. Particle deposition onto a substrate is affected by the flow dynamics inside sessile droplets and usually yields a ring shaped deposition process. [1] Being able to control it will enable to generate the desired deposition pattern. We therefore set out to measure and describe the drying kinetics under different conditions and used the developed expertise to control the deposition patterns of the cellulose nanocrystal films. Iridescent films with a uniform thickness were obtained by exerting control over the relative magnitude of Marangoni flow and the colloidal stability of the nanoparticles.



Figure. Photographs of cellulose nanocrystal films and uniform deposition by the means of Marangoni flow

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P₁₁

Self-assembly in Confined Spaces –Towards Functional Hybrid Materials

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Molecular self-assembly has attracted much attention as a bottom-up method for new functional nano-materials.^[1] The supramolecular approach is especially attractive, since it facilitates synthetic routes and yields dynamic functional aggregates combining properties of the individual building units with properties induced by the formation of the supramolecular entity.^{[2],[3]} The present work investigates the self-assembly of hydrogen-bonded liquid crystals^[4] in the confinement of chiral-nematic mesoporous silica films derived from cellulose nanocrystal (CNC) templating. The obtained hybrid materials^[5] revealed fast and reversible thermo- and photoresponsive switching of the photonic properties as proven by polarizing optical microscopy (POM), UV-vis and CD-spectroscopy.



Figure 1. Modular approach towards novel functional hybrid materials with tailor-made properties.

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P₁₂

Substrate effect on the colours of films dried from liquid crystalforming cellulose nanocrystal suspensions

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Nowadays the photonic properties of short-pitch cholesteric systems based on cellulosic biopolymers motivate innovative research for real products, targeting smart photonic applications. In this work, we produce thin films using cellulose nanocrystals (CNC) suspended in water.

The characteristic of the particles deposition process together with the self-assembly in the equilibrium suspension has a direct effect on the optical properties of the films obtained by drying 1. Preparation of the suspension (sonication, salt addition [2]), contact angle with the substrate [3] and humidity [4] also influence the optical properties.

Our experiments were conducted at ambient temperature and humidity. We investigate the film appearance on different types of substrate (hydrophilic and hydrophobic), for varying volume and concentration of the CNC suspension.



Figure. Drop casted CNC films after water evaporation, the CNC concentration increasing from 1 wt% (left) to 9 wt% (right). The volume of suspension is constant.

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