Active, self-motile, and driven emulsions

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Abstract

In this review, we focus on recent experiments involving transport and other dynamical aspects of emulsified droplets under non-equilibrium conditions. We include both active emulsions, where individual droplets develop self-propulsion or self-sustained motion at the expense of local energy sources, and driven emulsions, where droplets are activated through the local transduction of an external source. A common theme in the reported scenarios is the use of hybrid colloidal systems, where emulsions and liquid crystals are interfaced, providing with a rich scenario that features phenomena and mechanisms not found in traditional emulsions.

Keywords: Active soft matter, liquid crystals, driven colloids, electrokinetics, Lehmann rotation

1. Introduction

This review deals with nonequilibrium emulsions in which droplets of the dispersed phase are either self-propelled or indirectly driven by an external influence. Within a broader context, the systems we will address belong to the domain of active matter, although we want to differentiate between emulsified droplets that self-propel by converting stored or surrounding energy sources into directed motion (*true* active emulsions), and droplets that perform some sort of movement through the intervention of an external source (driven emulsions). An example of active emulsions is given by suspensions in oil of aqueous solutions incorporating in-vitro reconstitutions of cytoskeleton proteins, tubulin that self-assembles into microtubules, and kinesins, molecular motors that perform processive motion along the microtubules at the expense of surrounding adenosine triphosphate (ATP) as chemical fuel. The resulting material self-organizes into a dynamic state with self-sustained motion that may result, for instance, in the propulsion of these droplets, among other phenomena. An example of driven emulsions is given by suspensions of aqueous droplets in an immiscible anisotropic liquid, and propelled by an external alternating-current (AC) electric field due to asymmetric ionic flows creating around the droplets.

Many of the materials we will discuss incorporate, either as the disperse or as the continuous phase, liquid crystals, whose microscopic components (molecules or supramolecular aggregates) self-assemble as liquids with long-range orientational order, locally characterized by a vector denoted orientational or director field. There are two characteristics of these materials that will be relevant in several parts of this review: their tendency to organize into a homogeneous director field, and the anisotropy in their physico-chemical properties. Concerning the first characteristic, enclosing a liquid crystal into a droplet (usually spherical) necessarily distorts the homogeneous director alignment, which incurs into an energy cost and results in the formation of topological defects: regions where the liquid crystal order is lost to satisfy the shape of the enclosing boundary. Although the study of defect structure and dynamics is beyond the scope of this review, there will be situations where they offer us a handle to probe the dynamics in non-equilibrium situations, such during the study of active nematic emulsions. The second characteristic, the anisotropy of liquid crystals, is crucial to provide the driving mechanism of aqueous droplets emulsified in a liquid crystal under the influence of an AC electric field. The anisotropic dielectric permittivity and conductivity of the mesogen results in unbalanced ionic flows that break the fore-aft symmetry of the droplets, resulting in net propulsion.

The purpose of this review is to present examples from the past decade where emulsified liquid droplets are transported by different non-equilibrium mechanisms that result in either autonomous or driven motion. Many of those examples will correspond to systems that have been studied in our research group during these years. We will begin with active emulsions based on preparations that involve the celebrated kinesin/tubulin active fluid, which has been studied in direct or inverse oil/water emulsions, both with isotropic and anisotropic liquids. This system is one of the current paradigms in active soft matter bringing together colloidal scientists and biologists in the quest to understand, for example, intracellular transport phenomena. We will next revise the autonomous or driven motion in emulsions of non-biomimetic origin, where either Marangoni flows or liquid-crystal-enabled electrokinetic phenomena are at play. The reported systems and processes unveil new strategies for the controlled transport of cargo or reactants in confined environments. Finally, we will briefly describe a lesser known phenomenon, the so called Lehmann rotation, a crossed effect in non-equilibrium thermodynamics in which a heat flux exerts a mechanical torque in droplets of chiral liquid crystals.

2. Active emulsions

2.1. Active nematic mixture from microtubules and kinesins

Before reviewing experimental realizations of the concept of *active emulsions*, and later comment on some present developments and future perspectives this concept brings about, let us start by briefly introducing the specific active preparation in which active emulsions have been carried out so far. As a matter of fact, the chosen active mixture is one of the most paradigmatic and versatile examples of an active soft-condensed system [1]. Originally proposed by the group of Dogic near ten years ago [2], it consists of a colloidal (lyotropic) liquid crystal that is self-assembled as a minimal *in-vitro* reconstitution of the cytoskeletal milieu. Its three essential ingredients are: short stabilized microtubules (MTs), around one micron long, biotinylated kinesins, that act as molecular motors moving on microtubules, and a non-specific and non-absorbing depleting agent (PEG), that favors microtubule bundling (see Fig.1(a)). Although in the most recent developments it is being mostly prepared as a quasi-two-dimensional interfaced active film, the system was originally designed as a three-dimensional gel [3] in aqueous bulk solutions [2, 4].

Dimeric kinesins generate sliding forces between microtubules of opposite polarity, whereas no sliding force is induced between microtubules of the same polarity. Acting on bundled MTs, paired kinesins introduce local shear (extensile) stresses. Bundle dynamics thus undergo cyclic phases of extension, buckling, fracture and recombination. Permanent reconstitution of the network is accompanied by streaming currents that permeate the active gel system-wide.

The material can be made denser after being depleted towards an oily interface stabilized with a Polyethylene Glycol (PEG)-based surfactant. In this way, bundles conform textures that display a remarkable orientational order, albeit ruptured locally by a considerable number of topological defects. This symmetry qualifies the preparation as a (two-dimensional) *active nematic* (AN) [5] (see Fig.1(b)) . Correspondingly, the concurrent defects bear topological semi-integer ($\pm 1/2$) charges. Similarly to the gel preparation, active nematic textures appear permanently stirred by seemingly chaotic flows in a state often qualified of active turbulence, a concept that has attracted a wide attention in the field of active matter (for experimental references see [6, 7] in the context of microtubule-based AN, but also [8] in bacterial baths, and [9] for cell tissues. A numerical simulation-based approach to AN turbulence can be found in [10]). In the steady state, the spatial arrangement of the turbulent active nematic is characterized by a length scale in the colloidal domain (the *active length scale*, typically a few tens of microns) and it determines, for instance, the average distance between neighboring defects, but it will also be crucial when geometrical confinement is imposed during emulsification.

2.2. Active emulsions in isotropic oils

Apart from this conventional preparation at planar oily interfaces, the original paper [2] also reported an obvious extension that consists on encapsulating the active gel within droplets, by realizing water-in-oil active emulsions of the cytoskeleton protein mixture. There are at least two arguments that justify this interest. First and most obvious, to see whether the AN can be formed at all at these non-planar interfaces, given the intrinsic stiffness of the nematic material. Second, to see how defects in the system, and their associated charge, adapt to the constraint imposed by the topology of a closed curved interface.

In response to the first question, the AN effectively forms and triggers cortical flows for all but the smallest droplets (above a few tens of microns in diameter). In fact, bounded streaming currents are observed to be very much alike to the AN when evolving within planar interfaces. Moreover, when in frictional contact with a hard surface, internal flows drive the motility of the droplets (see Fig.1(c)). No trend of regular motion is identified for the biggest specimens, of sizes much larger than the active length scale. However, for droplets with intermediate size typically below a hundred microns according to our own observations (a few times the active length scale), this motility can show a rather periodic trend. The way to interpret this striking result is in fact related to the second previously posed question.

It is well-known in a classical soft-matter context, that nematic arrangements on closed curved surfaces are globally frustrated and, thus, unavoidably generate local defects with corresponding topological charges s_i. The total topological charge associated to the defect-populated surface is expressed in terms of the so-called Euler characteristics χ (Poincaré-Hopf theorem). On the other hand, according to the Gauss-Bonnet formula, the surface Euler characteristics is evaluated as

$$\chi = (1/2\pi) \int K dA,$$

where $K = (R_1 R_2)^{-1}$ denotes the Gaussian curvature, written in terms of the principal radii of curvature of a curved surface, and A is the surface area. For a sphere of radius R, $\chi = 2$ [11]. The simplest way to satisfy this constraint when only semi-integer defects are present is achieved by splitting the total $+2$ charge among four topological $+1/2$ defects.

This naturally applies also to an active nematic, with the obvious difference that in this case defects are intrinsically propelling on the curved surface. In equilibrium situations it is known that defect arrangements may be degenerated. The final adopted configuration, minimizing the free energy of the two-dimensional cortical nematic phase, depends on the relation of elastic constants. Under the usual assumption of equal elastic moduli for bend and splay distortions, the chosen arrangement corresponds to the four $+1/2$ defects located at the vertices of a tetrahedron inscribed within the sphere. This result was theoretically predicted in a couple of papers by Lubensky and Nelson [12, 13] and further experimentally confirmed for spherical (passive) nematic shells by Lopez-Leon et al. [14]. This result admits a straightforward interpretation since defects located at the corners of the tetrahedron maximize their mutual separation, minimizing in this way the elastic distortions within the liquid crystal matrix, and in turn the pair-repulsion forces self-exerted between defects. The periodic trend observed in the droplet motion would be then interpreted as the result of the active defect motion connecting complementary tetrahedral con-

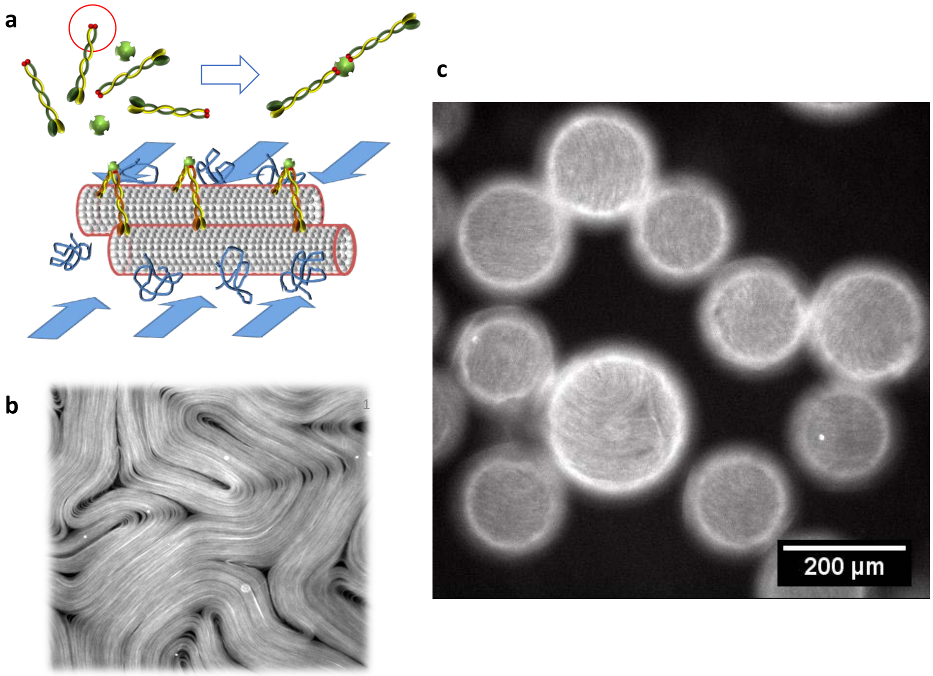

Figure 1: **Active nematic droplet emulsified in an isotropic oil.** **a** Components of the active system. Kinesin motors dimerize using streptavidin. Microtubules are mixed with the kinesin dimers and the system is condensed using a depleting agent. **b** The aqueous active mixture concentrates at an oily interface, resulting in an active nematic in the turbulent regime. The image is a fluorescence micrograph of the usual textures of the active nematic assembled on a flat interface. **c** Water-in-oil droplets encapsulating the active preparation, which forms spherical active nematic shells (unpublished data).

figurations with an intercalated planar disposition of the motile defects. The frequency associated to this dynamic mode depends on the activity parameter (essentially a measure of the ATP concentration) and the droplet radius. A similar dynamics was originally reported in the similar context of active vesicles [15], and corroborated later on with particularly dedicated numerical simulations [16].

An alternative to the water-in-oil active emulsions reviewed so far is to consider the reverse formulation, i.e. oil-in-water preparations, still employing the aqueous active micrototubule/kinesin as driving solution. Our group is presently investigating this approach following different perspectives, using glass-capillary-based microfluidic strategies for monodisperse emulsion fabrication [17]. A direct preparation involves the use of droplets of an isotropic compatible oil and disperse them in an active gel. Passive drops are supposed to display enhanced motility, driven by the self-sustained streaming currents that permeate the active gel. We expect those driven droplets to display temporary super-diffusive modes extending simple Brownian dispersion. On top of that, specific depletion effects of the bundled microtubules should manifest for big enough droplets and in the presence of the PEGylated surfactans, with interesting dynamic patterns of surface defect motion and coupling between interacting active shells in tightly assembled droplets (see Fig. 2).

2.3. Active nematic emulsions

Research on active emulsions can be easily widened in scope by replacing the isotropic oil-based continuous phase with an anisotropic fluid, typically a thermotropic Liquid Crystal (LC) in its nematic phase. We will refer later on in Sect. 3 to other particularly interesting realizations of this class of *nematic emulsions* that have recently permitted to explore scenarios of driven, rather than autonomous, motility.

Let us introduce first some pertinent concepts that apply generically to colloids dispersed in nematic LCs (for a recent review of this topic see [18]). *Nematic colloids*, as they are known, bring about close-by localized defects when their dimensions are larger than the typical de Gennes-Kleman length of the colloid/LC mixture (this length is a classical concept in LCs expressing the ratio of an effective elastic constant and the anchoring energy density [19, 20, 21]). The symmetries and topologies of these defects depend on the size of the inclusions, and on the anchoring conditions of the LC at the colloid boundary, the latter easily tuned for specific applications. In the simpler situations, homeotropic (perpendicular) anchoring favors either hedgehog-like defects of dipolar symmetry [22], manifested as a localized neighboring hyperbolic singularity, or as extended disclinations of quadrupolar symmetry, wrapping the colloid in the form of Saturn rings [23]. Conversely, planar (tangential) anchoring induce surface-localized pairs of defects in a configuration known as double-boojum.

From the precedent considerations, it is clear that *active nematic emulsions*, the active counterparts of the nematic emul-

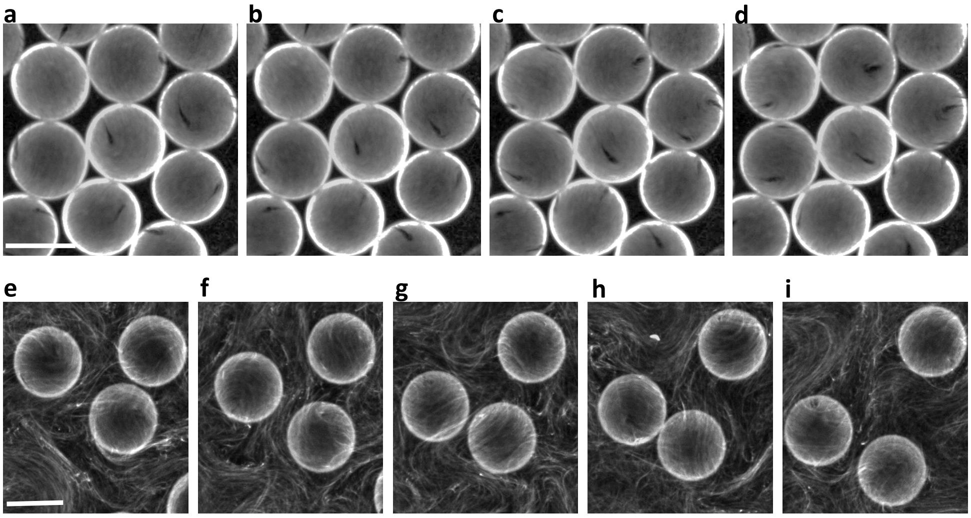

Figure 2: **Isotropic oil droplets emulsified in the kinesin/tubulin aqueous active material**. **a-d** Fluorescence micrographs when the active filaments have condensed as active nematic shells around the oil droplets (unpublished data). Some of the four self-driven +1/2 defects present in each shell are visible as dark regions devoid of fluorescent filaments. Elapsed times are 2s between each panel. **e-i** Fluorescence micrographs in the absence of condensation of the active filaments (unpublished data). Dispersed oil droplets are advected by the chaotic flow in the surrounding bulk active gel. Elapsed times are 15s between each panel. Scale bars, 50 μm.

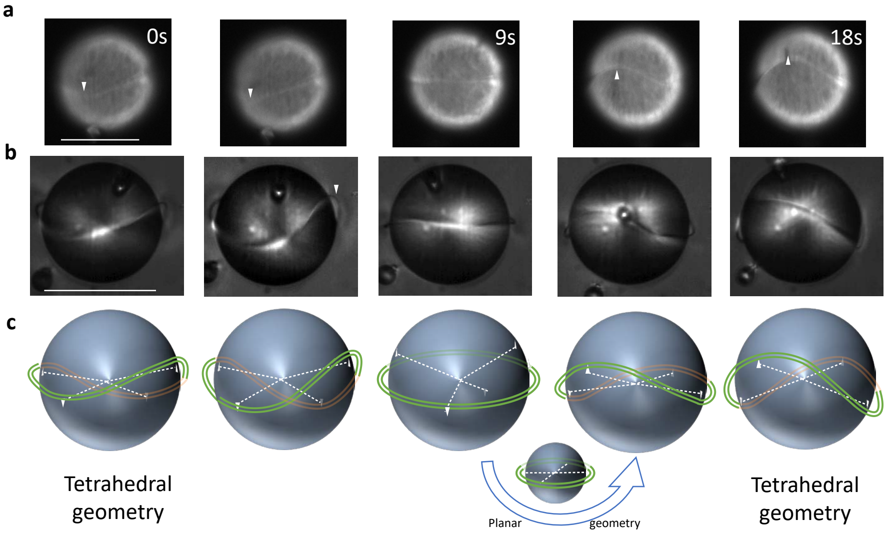

Figure 3: **Active nematic emulsions**. Tubulin-kinesin active mixture emulsified in a nematic liquid crystal oil results in droplets surrounded by a ring disclination (*Saturn ring*). The active nematic shell features self sustained motion that drives the disclination into periodic oscillations. **a** Fluorescence micrographs showing the active nematic shell and the bright disclination, which is pointed to by a white arrow. The elapsed times are displayed in some of the micrographs. **b** Brightfield micrographs under polarized light corresponding to the same phase in the oscillation of the disclination, which is pointed to by a white arrow in the second micrograph. **c** Sketch illustrating the configuration of the oscillating disclination in the corresponding micrographs in **a** and **b**. The position of the four self-driven +1/2 defects in the active nematic shell are indicated by white arrows. The four defects, which describe the vertices of a tetrahedron, transit through a co-planar arrangement parallel to the equilibrium position of the Saturn ring. Scale bars are 100 μm. Images correspond to unpublished data.

sions just mentioned, open new and interesting perspectives. Referring to the LC encapsulation of the microtubule/kinesin active material, the obvious question to be addressed is the eventual coupling between the active defects driving cortical flows inside the droplets and the passive singularities sitting around them in the surrounding passive LC. We analyzed this question in a couple of recent contributions published by Guillamat et al. [24], and Hardoüin et al. [25]. We briefly review on what follows the most paradigmatic scenario as reported in [24].

The dispersing medium of the aqueous active preparation is the hydrophobic thermotropic LC 4-pentyl-4-cyanobiphenyl (5CB) enclosed in a closed cell of 140μm gap between two parallel glass plates treated to impose a homogeneous in-plane alignment of the passive LC. Chemical functionalization at the droplet interface, yet compatible with the active material, permit to prescribe different anchoring conditions. More precisely, when using a PEGylated phospholipid, 5CB molecules organize an homeotropic anchoring, in the form of a localized ring disclination (Saturn ring). Conversely, using the more standard Pluronic surfactant (triblock copolymers with two PEG chains) one obtains planar alignment on the exterior of the active droplets and, correspondingly, double-boojum structures. On what follows we focus on the first referred situation that promotes the coupling of a passive Saturn-ring (SR) with the active defects. An account of other situations can be found in the original reference.

Bright-field and fluorescence imaging permit to track at any time the behavior of the SR disclination and to monitor the dynamics of defects in the active nematic (AN) shell, although only two of the four +1/2 active defects can, at most, be observed simultaneously (see Fig.3). A complete cycle of deformation is shown while active defects transit between the tetrahedral and planar configurations. Strikingly enough, some SRs, singularly under low activity, feature simple and periodic in time oscillations, while in other situations more complex regimes are observed with SR being distorted in multi-mode and/or non-periodic distortions, or even getting multiply wrapped around the droplet, and eventually, collapsed at one of the poles. Regular oscillations are a signature of the tight coupling between the AN dynamics, commented above in relation to pure active emulsions, and the passively dragged SR, and it is demonstrated only possible by a feedback mechanism that orients the AN defect manifold with respect to the SR. The mentioned variety of observed behaviors is likely to be due to both a quite wide range of droplet size distribution, added to the difficulty to guarantee a uniform partition of the components of the active sample and of the chemical surfactant. More details can be found in the paper published by Hardoüin et al. [25].

2.4. *Active vesicles*

In a separate, although close, context we already mentioned the possibility to encapsulate the microtubule-based active material inside lipid vesicles. As reported originally in the paper by Keber [15], the active mixtures were encapsulated into vesicles employing the continuous droplet encapsulation method (cDICE) [26]. Briefly, the protocol consists in using a cylindrical chamber, successively filled, ordered by decreasing density, with an aqueous glucose solution to collect the vesicles, a lipid-in-oil solution to saturate the oil/water (O/W) interfaces, and decane as the continuous phase in which droplet are produced. While the chamber is rotated, the aqueous solution containing the microtubules and motors is injected from a glass capillary by inserting its tip in the decane phase. Due to the centrifugal force, droplets detach from the tip and move through the lipid in oil solution where they get coated by a first lipid monolayer leaflet and then by a second, complementary lipid monolayer leaflet while crossing the O/W interface. The two monolayers zip together to form a bilayer.

Vesicles with sizes ranging from around ten to sixty microns were analyzed in Keber's paper [15]. Apart from observing the cyclic dynamics of four moving defects referred to above (see Fig. 4), authors were able to detect pronounced vesicle shape deformations originated by the active cortex flows. This was achieved by applying a hypertonic stress that caused a water efflux and subsequent vesicle deflation. The shape of slightly deflated vesicles continuously fluctuated around a mean spherical shape and was characterized by the continuous growth and shrinkage of the major and minor axis of an ellipse, with a periodicity set by the defect speed. In addition, these vesicles exhibited four motile protrusions that are tightly coupled to the dynamics of the underlying defects. Deflating the vesicles further causes a marked change in shape: The overall vesicle becomes anisotropic and motile, with filopodia-like protrusions growing in size and reaching lengths of tens of micrometers.

3. Emulsions showing autonomous and driven motion

3.1. *Self-propelled droplets driven by Marangoni flows*

Still within the context of autonomous motility, droplets self-propelling within another liquid phase due to surface tension gradients (Marangoni effect) have been mainly observed for two types of systems: surfactant-stabilized droplets, the surfactant layer of which is modified by chemical reactions, and surfactant-stabilized droplets undergoing a solubilization process. These paradigmatic situations and other less conventional have been widely reviewed in [27].

The first scenario is realized by Thutupalli et al. as squirming water droplets moving in an oil phase [28]. Propulsion arises due to the spontaneous bromination of a specifically chosen surfactant. The latter is abundant in the oil phase, such that the droplet interface is covered by a dense surfactant monolayer. The bromine fuel is supplied from inside the droplet and bromination proceeds mainly at the droplet surface. This results in a self-sustained bromination gradient which propels the droplet due to Marangoni stresses. This process was addressed theoretically by Schmitt et al. [29, 30].

The second situation is driven by solubilization processes favored by micellar assemblies. Two cases can be envisaged: oil droplets (eventually using a thermotropic LC in its nematic [31] or isotropic phase [32]) placed into an aqueous phase containing a surfactant at a concentration well above the critical micellar concentration, and with oil molecules being transferred

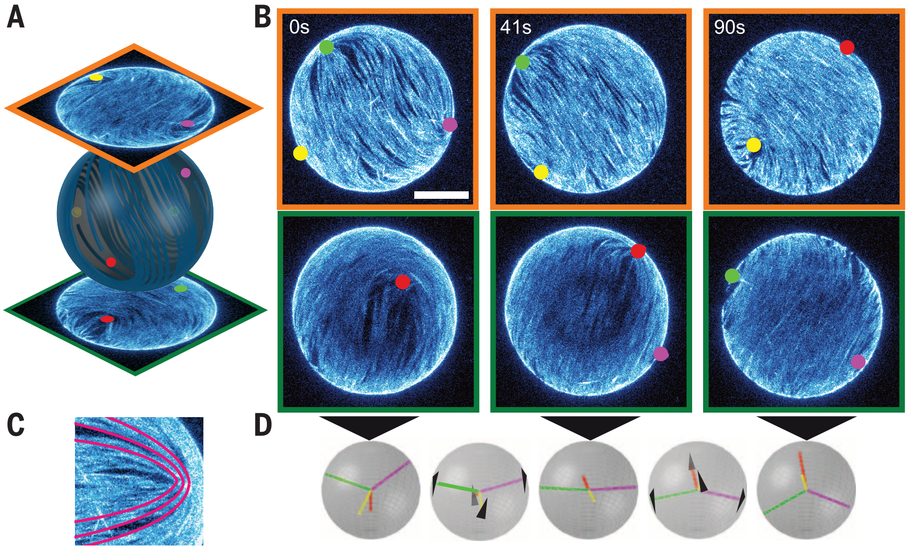

Figure 4: **Defect dynamics of an active nematic at the inner surface of a spherical vesicle**. (A) Hemisphere projection of a 3D confocal stack of a nematic vesicle. The positions of four +1/2 disclination defects are identified. (B) Time series of hemisphere projections over a single period of oscillation in which the four defects switch from tetrahedral (t = 0 s) through planar (t = 41 s) and back to tetrahedral (t = 90 s) configurations. Scale bar, 20 μm. (C) Comet-like +1/2 disclination defect. (D) Schematic of the defect configurations at the time points of (B) and intermediate times (t =24s, t = 65 s). The black arrowheads indicate the direction of defect motion. Image extracted from Keber et al. [15].

into the micelles. The reverse situation has been similarly designed with water droplets moving in an oil phase and inverse micelles [33, 34].

3.2. Droplets driven by means of electrokinetic effects

Although not self-propelled, a powerful transport alternative is to endow emulsified droplets with driven motility through electrokinetic effects. These processes are conventional in the study of colloidal systems [35]. The simplest and most common electrokinetic mechanism is the well-known phenomenon of electrophoresis in aqueous media driven by DC electric fields, in which the speed of the colloidal entity is proportional to the intensity of the driving field. A more subtle variant is known under the name of Induced Charge Electrophoresis (ICEP), which belongs to the class of Induced Charge Electrokinetic processes (ICEK). Its two more distinctive features are both its quadratic nature in relation to the applied electric field, thus permitting the use of alternating currents, and its tensorial nature, different with respect to the vectorial of normal electrophoresis, manifested in the fact that the direction of the driven velocity does not necessarily coincide with the applied field direction [36, 37]. ICEK phenomena are also possible in liquid crystals, here denoted LCEK, for Liquid Crystal-Enabled Electrokinetics [38, 39], with an important conceptual difference. In conventional ICEK charge separation is rooted in the colloid properties that break spatial symmetries locally around the charged interfaces. Contrarily, charge separation in LCEK is a pure solvent-based effect and it is mediated by local distortions in the orientational field of the liquid crystal itself due to the anisotropic properties of its electric permittivity and ionic conductivity [39]. Nonlinear electrophoresis in a nematic solvent (Liquid Crystal-Enabled Electrophoresis, LCEEP) was first reported by Lavrentovich et al. for metallic and dielectric particles [40]. Later on, and by referring to emulsified water droplets, Hernàndez-Navarro et al., contributed to the field with two original advancements summarized in a series of papers [41, 42].

In the first study [41], liquid droplets were confirmed to undergo directed transport, following exactly the same principle as for the solid particles considered in the original reference [40]. The LC was chosen to have a negative dielectric anisotropy (it aligns perpendicularly to the applied electric field). An electric field was applied perpendicularly to the sample by using indium-tin oxide (ITO) coatings at the top and bottom plates, thus inducing an in-plane alignment of the LC (planar alignment). Emulsified aqueous droplets were stabilized with sodium dodecyl sulphate (SDS), which, in turn, induces a homeotropic (perpendicular) alignment of the LC at the droplet interface. With this protocol, emulsions with droplet sizes ranging from 1 to 20 μm were studied. Typically, small droplets features hedgehog LC distortions and were motile due to the dipolar symmetry of such distortions, while larger ones induced Saturn-ring defects and were observed to be predominantly motionless due to their quadrupolar symmetry (see Fig.5).

Based on the same principle and extending it further, one should imagine the possibility to steer and dynamically self-assemble droplets, paralleling the development reported for the first time by Hernàndez et al. within our group [42] for solid inclusions. The idea there is to exploit photo-driven processes to promote prescribed alignment of the nematic phase, further translated in delicate steering and assembly modes of the driven colloids.

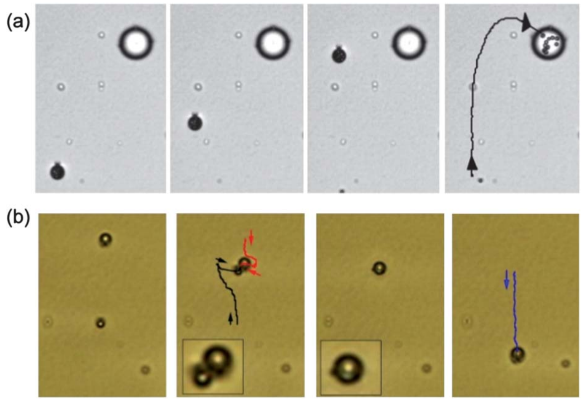

Figure 5: **Microfluidic transport in emulsions through Liquid Crystal-Enabled Electrophoresis LCEEP** . Image extracted from Hernàndez et al. [41]. **a** An aqueous microdroplet, 7.4 μm in diameter carries smaller solid microparticles along a themotropic liquid crystal layer. An AC electric field, perpendicular to the sample plane, provides with the propulsion mechanism. Along the way, the droplet merges with a fixed and larger aqueous droplet, thus releasing the solid cargo. **b** Two aqueous droplets, of diameters 2.7 μm and 3.7 μm, containing complementary reactants (hexacyanoferrate(II) and Fe^{3+} ions) are driven in opposite directions by the same mechanism as in **a**. Once they coalesce, following the tracked trajectories, they merge into a 4.3 μm droplet that acts as a micro-reactor, and that it is itself driven by the same propulsion mechanism.

4. Thermomechanical effects in liquid crystal emulsions

As a final example of emulsions that are driven into directed motion by a surrounding energy source we review a phenomenon found within the realm of chiral nematic liquid crystals. This materials are typically prepared by dissolving a small amount (typically less than 5% by weight) of a chiral dopant in a nematic liquid crystal. When droplets of these materials, also known as cholesteric liquid crystals, are placed in a temperature gradient, their microscopic constituents act as molecular rotors, and the orientational field inside the droplets is set into rotation (Fig. 6a). This phenomenon, known as the Lehmann effect, was demonstrated over a century ago, and has been recently rediscovered and studied in depth [43, 46, 47]. A practical reason for the current interest lays in the theoretically possible inverse effect, namely, the possibility to directionally drive heat away from a source in micro-confined environments through the rotation of chiral entities.

Our knowledge about the material requirements for Lehmann rotation to occur has been evolving during the past 10 years. The phenomenon is normally observed in cholesteric droplets in coexistence with the isotropic phase at the precise phase transition temperature. Although the thermomechanical coupling has been modelled in terms of the molecular level chirality, i.e., the presence of a chiral dopant, absence of a helical arrangement in the supramolecular orientational field hinders rotation. Moreover, it has been recently demonstrated that molecular-level chirality is not required, as long as a chiral orientational field is present. This has been demonstrated in recent experiments with droplets of a chromonic lyotropic liquid crytal [44] (Fig. 6b). Although the constituents are all achiral, droplet confinement and material properties results in helical arrangement of the orientational field, leading to Lehmann rotation in a temperature gradient.

The above observations are all reported for liquid crystal droplets at the temperature of coexistence with their isotropic phase, which diminishes the practical interest of such a phenomenon. Indeed, observation of the Lehmann thermomechanical rotation in liquid crystal droplets emulsified in an insoluble liquid would pave the way to potential applications, since dependence on a narrow temperature range would be absent. Interestingly, Lehmann rotation has only been obtained in emulsions where the liquid crystal and the surrounding fluids are partially miscible, as shown recently by Yoshioka and Araoka [48]. The authors found that, in this system, the effect is obtained at any temperature compatible with the cholesteric phase of the dispersed droplets, and the rotation speed is much faster under a given temperature gradient that those obtained in the conventional situation of droplets coexisting with the isotropic phase.

The underlying physical mechanism responsible for the Lehmann rotation is still not fully understood. For instance, it is unclear why the rotation is not possible when the surrounding fluid is immiscible with the liquid crystal inside the droplet. Interestingly, the rotation mechanism has been unveiled in the case of partially soluble emulsions. In this case, some of us recently showed that the giant temperature dependence of the interfacial tension triggers Marangoni flows under a vertical temperature gradient that generate convection backflows both inside and outside the droplets [45]. Seeding the surrounding liquid with tracer microparticles enables to clearly visualize such flows (Fig. 6c). Inside the droplet, these axisymmetric flows trigger the rotation of the chiral director field. A final consideration, relevant for the potential usefulness of this intriguing effect, and a matter of controversy, is whether the rotation of the orientational field triggers hydrodynamic flows. While initial experiments seem to point in this direction [46], recent studies have concluded that the Lehmann effect is a pure rotation of the orientational field. Be as it may, the emulsification of liquid crystals certainly leads to intriguing dynamic phenomena under non-equilibrium conditions.

5. Conclusions and Outlook

In this review, we have summarized recent research in which emulsions are studied under non-equilibrium conditions and from the perspective of dynamic phenomena arising at the level of individual or a reduced number of droplets. Many of the presented examples belong to the domain of active soft matter, in which droplet motion is the result of self-propulsion mechanisms, such as Marangoni flows arising from surfactant diffusion across the droplet interface, or the action of an active nematic shell either encapsulated inside an aqueous droplet in water-in-oil emulsions, or adsorbed onto the water/oil interface in reverse emulsions. Other examples involve driven droplets, propelled by a local mechanism that is fed by an external energy source, such as an oscillating electric field in the case of

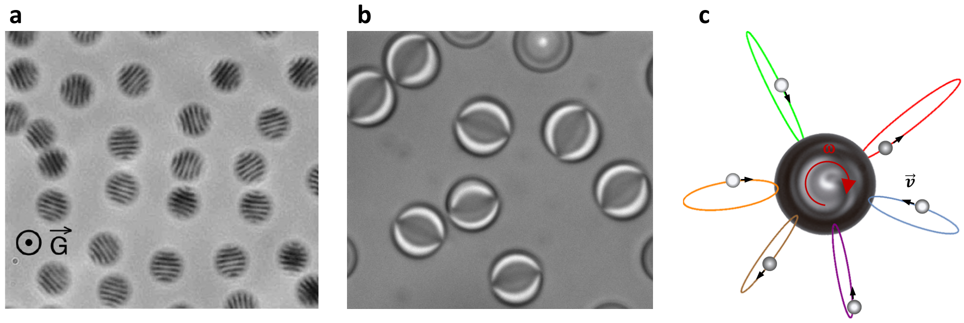

Figure 6: **Thermomechanical rotation in chiral microdroplets.** **a** Cholesteric thermotropic liquid crystal droplets, 12.5 μm in diameter, with a banded inner texture, as seen under brightfield microscopy. The texture, which results from helical pattern of the orientational field, rotates around the axis parallel to a temperature gradient, $\vec{G}$, as indicated in the micrograph. The image is adapted from Ref. [43]. **b** Droplets of the water-based, chromonic lyotropic nematic liquid crystal Sunset Yellow FCF that feature a twisted configuration of the orientational field are shown in coexistence with their isotropic phase. Under a temperature gradient (as indicated in **a**), they display Lehmann rotation [44]. Droplets are 50 μm in diameter. **c** Micrograph of a 30 μm droplet of a cholesteric thermotropic liquid crystal emulsified in a partially soluble fluorinated oil. In the presence of a temperature gradient (as indicated in **a**), Marangoni flows trigger hydrodynamic flows both outside (as illustrated by the sketched tracer particles) and inside the droplet, where these flows result in a rotation of the orientational field [45].

droplets propelled by liquid crystal-enabled electrokinetic drive or rotating chiral droplets in a temperature gradient.

As mentioned above, future perspectives involve studying collective effects and interaction among multiple active droplets. For this purpose, a first landmark would be to achieve a robust experimental procedure for the preparation of monodisperse samples of appropriately stabilized active droplets. In the context of emulsions with the kinesin/tubulin active material, conventional emulsifications protocols must be reassessed in the present context given the small amounts of the prized proteinic material one normally employs in standard procedures. Whether successfully prepared, a first envisaged scenario is the possibility to observe large-scale synchronization patterns subtended by the individual droplet-based oscillatory flows discussed above. Preliminary observations involving well known droplet-generating microfluidic techniques hold big promises to attain such a striking dynamical collective process under the non-equilibrium conditions secured by ATP feeding.

Active nematic emulsions featuring an arbitrary number of identical droplets could similarly be prepared. Paralleling the celebrated developments that have permitted in the past to assemble ordered arrays of nematic colloids [49], the goal here would be to see whether these arrangements are still compatible with the permanent activity and streaming flows operating inside the droplets. Adapting the optical manipulations that were required in equilibrium situations to entangle individual disclinations around solid colloids add here to the other challenges.

The scenario of collective effects can be also investigated in relation to liquid crystal-based droplets dispersed in an active gel. Again the motivation is diverse. From the one side, our previous research on planar interfaces of the AN material in contact with a layered smectic LC interface [50] evidence significant effects of the anisotropic interfacial rheological properties of the mesogen, resulting in a steering mechanism for active flows. Conversely, double emulsion droplets of smectic phases result in shells that evolve into ellipsoidal droplets [51]. By emulsifying such hydrophobic droplets in an aqueous active gel, and in the presence of a PEGylated surfactant, an outer ellipsoidal AN shell would form, thus permitting in this case to address not only rheological constraints, but additionally combined curvature and topological effects conditioning the textures and currents of the active material. This project is being pursued in collaboration with T. Lopez-Leon in ESPCI (Paris).

Extending the concept of active vesicles, and in collaboration with L. Casanellas at Univ. de Montpellier, an ongoing research aims at the controlled assembly of active giant unilamellar vesicles. The final goal is to elucidate whether the activity of individual vesicles is sufficient to induce the emergence of a collective motion within the tissue, which would be solely transmitted by vesicle-vesicle contacts, in absence of any external stimulus. Vesicle adhesion is mediated by ligand-receptor complexes (streptavidin-biotin complex [52], or DNA complementary strands [53]) at suitable concentrations [54]. The limited amount of active vesicles available, the fragility of the lipidic membrane, and the short life-time of activity are some of the experimental challenges to overcome in order to obtain these active biomimetic *tissues*.

Most of the reported studies in this review focus on fundamental aspects of the different dynamic mechanisms evidenced in emulsified droplets. Nevertheless, their understanding can pave the way for new strategies for the discrete transport and remote control of liquids at the femtoliter level for lab-on-a-chip applications, or for applications in biotechnoloy, autonomous microfluidic transport or soft robotics.

Conflicts of interest statement

The authors declare no conflicts of interest.

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Papers of particular interest, published within the period of review, have been highlighted as: * of special interest, ** of outstanding interest.

References

[1] D. Needleman, Z. Dogic, Active matter at the interface between materials science and cell biology, Nature Reviews Materials 2 (2017). doi:10.1038/natrevmats.2017.48.

[2] T. Sanchez, D. T. N. Chen, S. J. Decamp, M. Heymann, Z. Dogic, Spontaneous motion in hierarchically assembled active matter, Nature 491 (7424) (2012) 431–434.

[3] J. Prost, F. Jülicher, J. F. Joanny, Active gel physics, Nature Physics 11 (2) (2015) 111–117. doi:10.1038/nphys3224.

[4] G. Henkin, S. J. DeCamp, D. T. N. Chen, T. Sanchez, Z. Dogic, Tunable dynamics of microtubule-based active isotropic gels, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 372 (2029) (2014). doi:10.1098/rsta.2014.0142.

[5] A. Doostmohammadi, J. Ignés-Mullol, J. M. Yeomans, F. Sagués, Active nematics, Nature Communications 9 (1) (2018) 3246. doi:10.1038/s41467-018-05666-8.
** A review on active nematic fluids with up-to-date experimental realizations and modeling schemes.

[6] P. Guillamat, J. Ignés-Mullol, F. Sagués, Taming active turbulence with patterned soft interfaces, Nature Communications 8 (1) (2017) 1–8. arXiv:1611.06416, doi:10.1038/s41467-017-00617-1.
URL `http://dx.doi.org/10.1038/s41467-017-00617-1`

[7] B. Martínez-Prat, J. Ignés-Mullol, J. Casademunt, F. Sagués, Selection mechanism at the onset of active turbulence, Nature Physics 15 (4) (2019) 362–366. doi:10.1038/s41567-018-0411-6.
URL `http://dx.doi.org/10.1038/s41567-018-0411-6`

[8] H. H. Wensink, J. Dunkel, S. Heidenreich, K. Drescher, R. E. Goldstein, H. Löwen, J. M. Yeomans, Meso-scale turbulence in living fluids, Proceedings of the National Academy of Sciences 109 (36) (2012) 14308–14313. doi:10.1073/pnas.1202032109.

[9] C. Blanch-Mercader, V. Yashunsky, S. Garcia, G. Duclos, L. Giomi, P. Silberzan, Turbulent dynamics of epithelial cell cultures, Physical Review Letters 120 (20) (2018) 208101. arXiv:1711.01568, doi:10.1103/PhysRevLett.120.208101.
URL `http://arxiv.org/abs/1711.01568`

[10] L. Giomi, Geometry and topology of Turbulence in active nematics, Physical Review X 5 (3) (2015) 1–11. arXiv:1409.1555, doi:10.1103/PhysRevX.5.031003.

[11] R. D. Kamien, The geometry of soft materials: a primer, Reviews of Modern Physics 74 (October) (2002) 953–971.
URL `http://link.aps.org/abstract/RMP/v74/p953`

[12] T. C. Lubensky, J. Prost, Orientational order and vesicle shape, Journal de Physique II 2 (1992) 371–382.
URL `http://link.aps.org/abstract/RMP/v74/p953`

[13] D. R. Nelson, Toward a Tetravalent Chemistry of Colloids, Nano Letters 2 (10) (2002) 1125–1129. arXiv:0206552, doi:10.1021/nl0202096.

[14] T. Lopez-Leon, V. Koning, K. B. Devaiah, V. Vitelli, A. Fernandez-Nieves, Frustrated nematic order in spherical geometries, Nature Physics 7 (5) (2011) 391–394. doi:10.1038/nphys1920.

[15] F. Keber, E. Loiseau, T. Sanchez, S. DeCamp, L. Giomi, M. Bowick, M. C. Marchetti, Z. Dogic, A. Bausch, Topology and Dynamics of Active Nematic Vesicles, Science 345 (6201) (2015) 1135–1139. arXiv:15334406, doi:10.1126/science.1254784.
** First experimental report on active nematic vesicles. A gel composed of a mixture of microtubules and kinesins is encapsulated and results on active cortical flows. Characteristics of the flows are analized as well as large-scale droplet deformation.

[16] R. Zhang, Y. Zhou, M. Rahimi, J. J. De Pablo, Dynamic structure of active nematic shells, Nature Communications 7 (2016) 1–9. doi:10.1038/ncomms13483.
URL `http://dx.doi.org/10.1038/ncomms13483`

[17] A. S. Utada, E. Lorenceau, D. R. Link, P. D. Kaplan, H. A. Stone, D. A. Weitz, Monodisperse double emulsions generated from a microcapillary device, Science 308 (5721) (2005) 537–41.

[18] I. Muševič, Liquid Crystal Colloids, Springer, 2017.

[19] P. de Gennes, J. Prost, The Physics of Liquid Crystals, Clarendon, Oxford, 1993.

[20] M. Kleman, O. Lavrentovich, Soft Matter Physics: An Introduction, Springer, New York, 2003.

[21] P. Oswald, P. Pieranski, Nematic and cholesteric liquid crystals: Concepts and physical properties illustrated by experiments, Taylor and Francis, Boca Raton, 2005.

[22] P. Poulin, H. Stark, T. C. Lubensky, D. A. Weitz, Novel Colloidal Interactions in Anisotropic Fluids, Science 275 (March) (1997) 1770–1773.

[23] Y. Gu, N. L. Abbott, Observation of Saturn-Ring Defects around Solid Microspheres in Nematic Liquid Crystals, Physical Review Letters 85 (2000) 4719–4722.

[24] P. Guillamat, Ž. Kos, J. Hardoüin, J. Ignés-Mullol, M. Ravnik, F. Sagués, Active nematic emulsions, Sci. Adv. 4 (2018) eaao1470.
** First experimental report on active nematic emulsions. The active gel of microtubules and kinesins is emulsified with a thermotropic liquid crystal. Interesting features of the coupling between active and passive defects are described and analyzed with numerical modeling.

[25] J. Hardoüin, P. Guillamat, F. Sagués, J. Ignés-Mullol, Dynamics of Ring Disclinations Driven by Active Nematic Shells, Frontiers in Physics 7 (October) (2019) 1–9. doi:10.3389/fphy.2019.00165.

[26] M. Abkarian, E. Loiseau, G. Massiera, Continuous droplet interface crossing encapsulation (cDICE) for high throughput monodisperse vesicle design, Soft Matter 7 (10) (2011) 4610–4614. doi:10.1039/c1sm05239j.

[27] C. C. Maass, C. Krüger, S. Herminghaus, C. Bahr, Swimming Droplets, Annual Review of Condensed Matter Physics 7 (1) (2016) 171–193. doi:10.1146/annurev-conmatphys-031115-011517.

[28] S. Thutupalli, R. Seemann, S. Herminghaus, Swarming behavior of simple model squirmers, New Journal of Physics 13 (2011) 073021. doi:10.1088/1367-2630/13/7/073021.

[29] M. Schmitt, H. Stark, Swimming active droplet: A theoretical analysis, Europhys. Lett. 101 (4) (2013) 44008. doi:10.1209/0295-5075/101/44008.

[30] M. Schmitt, H. Stark, Marangoni flow at droplet interfaces : Three-dimensional solution and applications , Physics of Fluids 28 (2016) 012106. doi:10.1063/1.4939212.

[31] S. Herminghaus, C. C. Maass, C. Krüger, S. Thutupalli, L. Goehring, C. Bahr, Interfacial mechanisms in active emulsions, Soft Matter 10 (2014) 7008–7022. doi:10.1039/c4sm00550c.

[32] C. Jin, C. Krüger, C. C. Maass, Chemotaxis and autochemotaxis of self-propelling droplet swimmers, Proceedings of the National Academy of Sciences 114 (20) (2017) 5089–5094. doi:10.1073/pnas.1619783114.

[33] Z. Izri, M. N. Van Der Linden, S. Michelin, O. Dauchot, Self-propulsion of pure water droplets by spontaneous Marangoni-stress-driven motion, Physical Review Letters 113 (24) (2014) 248302. doi:10.1103/PhysRevLett.113.248302.

[34] C. D. Blois, M. Reyssat, S. Michelin, O. Dauchot, Flow field around a confined active droplet, Physical Review Fluids 4 (5) (2019) 54001. doi:10.1103/PhysRevFluids.4.054001.
URL `https://doi.org/10.1103/PhysRevFluids.4.054001`

[35] R. J. Hunter, Foundations of Colloid Science, Oxford University Press, 2000.

[36] T. M. Squires, M. Z. Bazant, Induced-charge electro-osmosis, Journal of Fluid Mechanics 509 (2004) 217–252.

[37] M. Z. Bazant, T. M. Squires, Induced-Charge Electrokinetic Phenomena : Theory and Microfluidic Applications, Physical Review Letters 92 (February) (2004) 066101. doi:10.1103/PhysRevLett.92.066101.

[38] O. D. Lavrentovich, Transport of particles in liquid crystals, Soft Matter 19 (2014) 1264–1283. doi:10.1039/c3sm51628h.

[39] O. D. Lavrentovich, Active colloids in liquid crystals, Current Opinion in Colloid & Interface Science 21 (2016) 97–109. doi:10.1016/j.cocis.2015.11.008.
URL `http://dx.doi.org/10.1016/j.cocis.2015.11.008`

[40] O. D. Lavrentovich, I. Lazo, O. P. Pishnyak, Nonlinear electrophoresis of dielectric and metal spheres in a nematic liquid crystal, Nature 467 (7318) (2010) 947–50.

[41] S. Hernàndez-Navarro, P. Tierno, J. Ignés-Mullol, F. Sagués, Ac electrophoresis of microdroplets in anisotropic liquids: transport, assembling and reaction, Soft Matter 9 (33) (2013) 7999–8004.
*Using the mechanism of nonlinear electrophoresis mediated by liquid

crystals, scenarios of transport of water droplets emusified with a nematic fluid are described.

[42] S. Hernàndez-Navarro, P. Tierno, J. A. Farrera, J. Ignes-Mullol, F. Sagués, Reconfigurable swarms of nematic colloids controlled by photoactivated surface patterns, Angew. Chem. Int. Ed. Engl. 53 (40) (2014) 10696–700.

[43] P. Oswald, A. Dequidt, Measurement of the continuous lehmann rotation of cholesteric droplets subjected to a temperature gradient, Physical Review Letters 100 (21) (2008) 217802.

[44] J. Ignes-Mullol, G. Poy, P. Oswald, Continuous rotation of achiral nematic liquid crystal droplets driven by heat flux, Phys Rev Lett 117 (5) (2016) 057801.

[45] P. Oswald, J. Ignes-Mullol, A. Dequidt, Lehmann rotation of cholesteric droplets driven by marangoni convection, Soft Matter 15 (2019) 2591–2604.
* The mechanism underlying the first manifestation of Lehmann rotation in an emulsion by Yoshioka et al is unveiled in this manuscript. Even in this case, the rotation itself seems to be a pure rotation of the local orientational field.

[46] J. Yoshioka, F. Ito, Y. Suzuki, H. Takahashi, H. Takizawa, Y. Tabe, Director/barycentric rotation in cholesteric droplets under temperature gradient, Soft Matter 10 (32) (2014) 5869–77.

[47] P. Oswald, A. Dequidt, G. Poy, Lehmann effect in nematic and cholesteric liquid crystals: a review, Liquid Crystals Reviews 7 (2) (2019) 142–166.
** An up-to-date overview of the different manifestations of the Lehmann rotation, a discussion of the current knowledge and an account of the challenges ahead.

[48] J. Yoshioka, F. Araoka, Topology-dependent self-structure mediation and efficient energy conversion in heat-flux-driven rotors of cholesteric droplets, Nat Commun 9 (1) (2018) 432.

[49] I. Muševič, M. Škarabot, U. Tkalec, M. Ravnik, S. Žumer, Two-Dimensional Nematic Colloidal Crystals Self-Assembled by Topological Defects, Science 313 (August) (2006) 954–959.
* The first example of Lehmann rotation in an emulsion is presented and analyzed in the experiments within this publication. The coupling appears to be much more efficient than in the standard experiments.

[50] P. Guillamat, J. Ignés-Mullol, F. Sagués, Control of active liquid crystals with a magnetic field, Proceedings of the National Academy of Sciences of the United States of America 113 (20) (2016) 5498–5502. doi:10.1073/pnas.1600339113.

[51] T. Lopez-Leon, A. Fernandez-Nieves, M. Nobili, C. Blanc, Smectic shells, Journal of Physics Condensed Matter 24 (28) (2012). doi:10.1088/0953-8984/24/28/284122.

[52] D. A. Noppl-Simson, D. Needham, Avidin-biotin interactions at vesicle surfaces: Adsorption and binding, cross-bridge formation, and lateral interactions, Biophysical Journal 70 (3) (1996) 1391–1401. doi:10.1016/S0006-3495(96)79697-2.
URL `http://dx.doi.org/10.1016/S0006-3495(96)79697-2`

[53] P. A. Beales, T. Kyle Vanderlick, Specific binding of different vesicle populations by the hybridization of membrane-anchored DNA, Journal of Physical Chemistry A 111 (49) (2007) 12372–12380. doi:10.1021/jp075792z.

[54] O. A. Amjad, B. M. Mognetti, P. Cicuta, L. Di Michele, Membrane Adhesion through Bridging by Multimeric Ligands, Langmuir 33 (5) (2017) 1139–1146. doi:10.1021/acs.langmuir.6b03692.