A review is given of the field of mineral colloidal liquid crystals: liquid crystal phases formed by individual mineral particles within colloidal suspensions. Starting from their discovery in the 1920s, we discuss developments on the levels of both fundamentals and applications. We conclude by highlighting some promising results from recent years, which may point the way towards future developments.

1. Introduction

In this contribution, we discuss the field of mineral colloidal liquid crystals (MCLCs), which we define as phases with a liquid crystal (LC) (super)structure formed by individual mineral particles within colloidal suspensions (for extensive reviews, see [1–3]). Since LCs display a partially ordered long-range structure, which always involves orientational order, these colloidal mineral particles necessarily have to be sufficiently anisometric (i.e. of different size in at least two different directions). Such mineral colloidal particles can be of both natural and synthetic origin.

Naturally occurring clays show beautiful examples of sheet (or plate)-like particles (e.g. bentonite), rod-like particles (e.g. sepiolite) or even tubular particles (e.g. imogolite). While some of these systems do form LCs when brought into suspension, often the predicted LC formation is pre-empted by a sol/gel transition. An example is discussed in more detail in the paper by Cui et al. [4]. Colloidal mineral particles can also be synthesized by traditional inorganic precipitation reactions, sometimes followed by a phase transformation, and more recently by metallo-organic methods, ‘soft chemistry’ [5] or compartmentalized growth.
The crowning event of the early years of MCLCs is without doubt Onsager’s explanation in the 1940s of the formation of a nematic phase—a decrease in excluded volume compensating for a loss of orientational entropy. Not only does Onsager’s explanation of the formation of a nematic phase remain a cornerstone in the field of MCLCs after 70 years, its extension by computer simulations has considerably widened the scope of the original argument. Furthermore, it has enriched several fields. One may think of the implications of Onsager’s concepts for the study not only of colloids in general (potential of mean force), but also of statistical mechanics in general (entropy-driven phase transitions).

The number of MCLCs has steadily increased. By tuning the size and shape of the particles and their mutual interactions, novel and interesting phase behaviour has been observed. Moreover, in the last decade, the potential of wet chemical synthesis routes to provide high-aspect-ratio colloidal nanorods with interesting directional, optical, electronic and catalytic properties has grown drastically.

We discuss the present state of MCLCs using examples partly based on our own work. Building on these developments, we outline new frontiers where we feel future (r)evolutions in the field may take place. From a fundamental point of view, this includes the observation that, by tuning the long-range repulsion, LC phases are realized (lamellar and smectic B (SmB) phases), which so far have not been predicted by theory or simulation. From the point of view of applications, LC formation in principle provides a simple and cost-efficient strategy to produce organized structures of nanorods. While some promising steps have been made towards using this to realize interesting devices involving nanorods with special directional, optical, electronic and catalytic properties, commercial exploitation is still in its infancy.


Within the first half of the last century, important progress in the field of MCLCs had already been made by Zocher joining the group of Freundlich at the Kaiser-Wilhelm-Institut für Physikalische Chemie und Elektrochemie in Berlin-Dahlem, Germany. In a seminal paper of 1925—only a few years after the classification of LC phases was introduced by Friedel [6]—Zocher [7] recognized the formation of nematic LCs in the guise of birefringent spindle-shaped areas (which subsequently became known as tactoids) in colloidal suspensions of what he presumed to be needle-like vanadium pentoxide (V₂O₅) particles. Following up on his previous work on temporary alignment leading to streaming birefringence at lower concentrations [8], he now recognized these tactoids to be orientationally ordered (nematic) droplets of higher particle density within an isotropic background of lower particle density deformed by the elastic forces acting within the anisotropic structure of the tactoids. He argued that, in low-molecular-weight LCs, these elastic forces are generally too small to deform the spherical shape caused by the surface tension of droplets. Zocher also noticed so-called atactoids consisting of spindle-shaped areas of dilute isotropic droplets deformed by the elastic forces in the surrounding nematic region. In a subsequent paper with Jacobsbohn [9], Zocher placed his findings on V₂O₅ particles in the context of the famous work on spherical colloidal particles by 1926 Nobel Prize laureate Jean Perrin [10], discussing the occurrence of Brownian motion, sedimentation (profiles) and deviations from Van’t Hoff’s ideal (gas) law at higher concentrations. However, although he also considered repulsive forces protecting the colloidal particles against coagulation, he explained the occurrence of phase coexistence by explicitly invoking attractive forces as an anisotropic analogue of the liquid–vapour coexistence described by van der Waals. In contrast to the situation of two immiscible fluids, he also noted the completely flat interface between the phases after complete sedimentation of the tactoids, which he ascribed to a very low interfacial tension.

In the same paper [7] describing his clear recognition of the isotropic–nematic (I–N) phase transition in suspensions of V₂O₅, Zocher also reported the observation of a smectic phase in 15–30 year old suspensions of iron (hydr)oxide. He deduced this from the observation of iridescent layers (‘Schillerschichten’) in the bottom layer of the suspension, which—when mixed
into a homogeneous dispersion with some drops of the isotropic upper layer—spontaneously reformed in between two microscope slides. Zocher assigned the bright colours characterizing these ‘Schillerschichten’ to Bragg reflection of visible light on regularly stacked layers of supposedly plate-like FeO(OH) particles (more particularly identified by X-ray diffraction on the dispersion by Böhm [11] as the mineral goethite). In 1930, Zocher & Heller [12] pursued this topic trying to synthesize particles by hydrolysing iron chloride in a better controlled way. This indeed again led to the formation of ‘Schillerschichten’. Zocher correctly referred to these as (the colloidal analogue of) the smectic phase, although he and his co-workers assumed that FeO(OH) particles were plate-like, whereas these turned out to be rod-like β-FeO(OH) as described later. In 1937, Coper & Freundlich [13], former collaborators of Zocher, reported the first nematic phase in suspensions of goethite, α-FeO(OH).

In the meantime, Bawden et al. had also observed I–N phase separation in suspensions of tobacco mosaic virus (TMV) [14]. Although of course not of mineral origin, suspensions of rigid, cylindrical, rod-like TMV behave completely analogously and this observation turned out to be of crucial importance for the historical development (for an extensive review of these and other LC viruses, see [15,16]).

All the previously cited work and many more experiments on concentrated suspensions and gels of charged colloids were extensively discussed in an ambitious paper by Langmuir [17], which was part review, part theoretical analysis but also reported new experiments on plate-like bentonite. In this clay suspension, Langmuir observed a clear phase separation at around the 2 per cent volume fraction, which strongly suggested an I–N coexistence although it easily formed gels, and Langmuir primarily discussed it in terms of three-dimensional order.

Inspired by the experiments collected by Langmuir—although only explicitly citing his paper—Onsager announced a theory of the I–N transition in 1942 in a remarkable abstract [18], postponing the publication of his full theory to 1949 [19]. In a both physically and mathematically very lucid and elegant analysis, he showed that LC ordering can occur in suspensions in which interparticle forces are purely repulsive. The first-order I–N transition for hard anisometric particles can be understood as the result of a competition between orientational entropy and free volume entropy (using a virial expansion for the excluded volume interactions): a decrease in orientational entropy is compensated by an increase in the translational entropy owing to a reduced excluded volume between the particles within the orientationally ordered nematic phase at higher volume fractions. Onsager argued that his theory became increasingly accurate for increasingly anisometric rod-like particles. He also indicated that the I–N transition that he found for thin rods could be mapped on the case of thin plate-like particles, although conceding that in this case his theory became more approximate owing to the fact that plates have two long axes instead of only one. From Onsager’s work, it follows that ordering can be driven by entropy alone, a concept which remained counterintuitive for a long time but has proved to be very important in statistical mechanics and extends far beyond LC phase transitions. The use of the potential of average/mean force introduced by Onsager and applied in this paper to provide a description of electrostatic double-layer repulsion for charged colloids dominates modern colloid science.


In the decades after the publication of Onsager’s theory, the activity on viruses continued, for example, with the subsequent discovery of smectic phases in suspensions of TMV by Oster in 1950 [20], later supplemented by LCs found in other rod-like (although semiflexible) viruses such as fd virus [21]. However, there was little activity to prepare new rod- or plate-like mineral colloids with the exception of continued efforts on Zocher’s part leading to his discovery of a nematic phase in colourless suspensions of fibrous rod-like γ-AlO(OH) particles [22], independently found by Bugosh [23].

Within the same period, the interest in phase transitions in suspensions of spherical colloids steadily grew. The preparation of monodisperse spherical polymer colloids (latices) in the 1950s led to the observation of colloidal crystals [24] a few years after their viral counterpart was
found in Tipula iridescent virus [25]. Zocher followed these developments closely and related them to superstructures identified in his dispersions of anisometric particles [26]. In parallel with this, early computer simulations starting at the end of the 1950s by Alder among others [27,28] demonstrated a fluid–crystal transition in a system of hard spheres. Even so, it took until the 1970s before the connection between an earlier theory by Kirkwood [29], computer simulations and observations of colloidal crystals was made, when the Japanese school coined the name Kirkwood–Alder transition [30]. Soon afterwards, Hachisu et al. [31] were the first to suggest a connection between Onsager’s work and this ‘Kirkwood–Alder transition’.

In the late 1970s, strong interest developed in the structure and dynamics of concentrated colloidal suspensions as model liquids to approximate hard spheres [32,33]. This in turn generated interest in the preparation of monodisperse spherical (model) colloids with well-defined size and tuneable interactions.


Inspired by the developments in the field of concentrated suspensions of spherical colloids exhibiting the remarkable phenomenon of the spontaneous transition from fluid-like structures to crystal structures, renewed interest in the field of mineral colloidal crystals can be seen as the result of a combination of several factors:

1. Although in early work the nature of the LC phase was often correctly identified, the introduction of electron microscopy (EM) and small-angle X-ray scattering (SAXS) often led to better identification of particle shapes.
2. A wider range of ‘model’ systems were developed in which the particles have known shapes, sizes, better controlled polydispersity and (tuneable) interactions.
3. Techniques such as EM, advanced optical microscopy and the scattering of X-rays, neutrons and light were more widely used to study LC phases.
4. The continued development of statistical mechanics, in general, and advances in liquid state theories, in particular, created powerful concepts and tools which were increasingly supported and guided by computer simulations.

In the following, we describe how this revitalized the field of MCLCs.

(a) Rods: theory, simulation and selected experimental systems

(i) Theory and computer simulation

Extensions of the Onsager theory. Although the results of Onsager’s theory are of great fundamental and methodological interest, they refer strictly speaking to infinitely thin hard rods. Hence, the applicability of the theory to experimental results is very limited. In real suspensions of rod-like particles, we have to take into account one or more of the following aspects:

— particles are not infinitely thin (or at least their aspect ratio $L/D \gg 1$, where $L$ is the rod length and $D$ the rod diameter);
— particles may be polydisperse (mineral particles in particular);
— particles are not hard but may show (long-range) repulsions and attractions; and
— particles (such as viruses or polymers) may be semiflexible.

In his original paper [19], Onsager had already indicated how to address the issues of particle repulsions and polydispersity and analysed the influence of the aspect ratio. All issues raised above have already been comprehensively reviewed by us [34]. A remarkable result is that for sufficiently polydisperse particles two nematic phases may be in equilibrium with an isotropic phase [35]. This has indeed been observed experimentally [36,37], as we will discuss below.
As mentioned before, in the early days, Zocher [7,12] observed smectic phases in suspensions of iron (hydr)oxide and by 1983 Maeda & Hachisu [38] proved by optical microscopy and EM that the smectic phase of $\beta$-FeO(OH) consisted of layers of perpendicular rod-like particles of square cross section interacting under unmistakably predominant repulsive conditions. However, until the mid-1980s, it was generally accepted in the literature that smectic LC ordering demanded that attractive forces operate between the particles. This observation raised the fundamental question of whether a thermodynamic stable smectic phase can occur in a system of particles with purely repulsive interactions. This question was addressed with computer simulations by Frenkel et al. [39], who presented convincing evidence that hard spherocylinders (of aspect ratio 6) with both translational and orientational freedom can form a thermodynamically stable smectic phase. This issue was further addressed by McGrother et al. [40] and Bolhuis & Frenkel [41] for a wide range of $L/D$ values. A remarkable result of these simulations is that the smectic phase—appearing first for spherocylinders with aspect ratio 4.1—requires fewer anisometric particles than the nematic phase where the aspect ratio should be least 4.7 (figure 1).

(ii) Selected systems of rod-like particles

Colloidal boehmite ($\gamma$-AlO(OH)) rods. Colloidal boehmite has been studied for a long time [11], and is of considerable industrial importance as a catalyst carrier. Incidentally, $\gamma$-AlO(OH) is named boehmite after Böhm [11], although he denoted it as bauxite at the time of his collaboration with Zocher around 1925. Inspired by Zocher & Török’s [22] and Bugosh’s [23] work in the early 1960s, Buining et al. [42] explored the preparation of colloidal boehmite rods by hydrothermal treatment of aluminium alkoxide precursors in the early 1990s. Colloidal boehmite rods with an average particle length $L$ between approximately 100 and 400 nm (controlled by varying the initial amounts of alkoxide and acid) and aspect ratio $L/D$ varying from 10 to 30 were obtained in this way, showing (some) polydispersity in both the particle length and diameter.

Subsequently, these boehmite particles were sterically stabilized by grafting a layer of low-molecular-weight poly(isobutene) (PIB) molecules on their surface [36]. Dispersed in cyclohexane, the sterically stabilized boehmite rods repel each other as a result of steric
hindrance of the grafted polymer chains and can be modelled as nearly hard rods. Above a critical concentration dispersion, these sterically stabilized boehmite rods show a fast I–N phase transition. After months of standing, a second nematic phase emerged in the biphasic dispersion. Comparison of the coexisting concentrations with Onsager’s theory extended to a (bidisperse) mixture of two particle lengths [35] gives remarkably good agreement. This study shows that Onsager’s theory extended to take into account polydispersity applies well to experimental results.

Colloidal β-FeO(OH) rods

In a remarkable study, Maeda & Hachisu [38,43] proved by optical microscopy and EM that in low-salt (10$^{-4}$ mol l$^{-1}$ or less monovalent salt) aqueous suspensions of β-FeO(OH) colloids a biphasic equilibrium arises between an isotropic and a smectic phase, the latter consisting of layers of perpendicular rod-like particles of square cross section. The ratio of the bare length, $L = 350$ nm, to the bare thickness, $D = 60$ nm, is approximately 6. However, taking into account the double-layer repulsion, the effective thickness may increase by 30 nm, so that the length-to-effective diameter ratio drops below 4, and hence a direct transition from the isotropic to the smectic phase takes place as expected from the computer simulations. It testifies to the insight of Hachisu that, long before the computer simulations revealed this feature, he surmised that the absence of the nematic phase was due to the fact that the particles were not sufficiently anisometric.

The work of Maeda and Hachisu was elaborated upon in a number of publications by Maeda and Maeda. They used atomic force microscopy to investigate the smectic structures of β-FeO(OH) rods [44,45], confirming the earlier results of Maeda and Hachisu. Furthermore, they investigated the role of long-range forces in smectic ordering [46] by changing pH over a wide range. Finally, with optical microscopy, they observed the nucleation and growth of the smectic phase [47]. In pre-smectic transition regions, lateral clustering of the particles and subsequent layering of the clusters were observed, representing a novel pathway to phase formation.

Colloidal silica rods

A beautiful example of the development of the ever wider range of ‘model’ systems in which the particles have known shapes, sizes and (tuneable) interactions is provided by the synthesis of almost monodisperse, rod-like silica colloids by Kuijk et al. [48]. Bullet-like silica rods were produced with diameters of 200 nm and higher and lengths up to 10 μm, resulting in aspect ratios from 1 to 25. The growth mechanism of these rods involves emulsion droplets inside which silica condensation takes place. Owing to an anisotropic supply of reactants from the droplet to the nucleus, the nucleus grows to one side only, resulting in rod (bullet) formation. In concentrated dispersions, these rods self-assemble into LC phases, which can be studied quantitatively on the single particle level in three-dimensional real space (figure 2), since the particles can be fluorescently labelled in various ways. For a system of these silica rods with $L/D = 5$ in sedimentation equilibrium, a multi-phase equilibrium involving an isotropic, nematic, smectic and SmB phase was observed [49]. While the I–N–Sm equilibrium follows from the equations of state provided by computer simulations [41], the SmB phase has so far not been predicted by theory or simulations in systems of rod-like particles with purely repulsive interactions. Kuijk [49] puts forward as a possible explanation that the SmB phase is the result of the length polydispersity of the rods, which prevents them from forming a truly three-dimensional-ordered crystal phase.

(b) Plates: theory, simulation and selected experimental systems

(i) Theory and computer simulation

As mentioned in §2, the work of Langmuir [17] was an important source of inspiration for Onsager [19] in his theoretical treatment of the I–N phase transition in systems of anisometric...
particles with purely repulsive interactions. Langmuir recognized that the particles of the clay he used (referred to by Langmuir as Californian bentonite, but which is now recognized to be hectorite [50]) were flat plates or discs. While the theory of Onsager is quantitatively correct only for (infinitely) long hard thin rods, the Onsager argument that the first-order I–N transition for hard anisometric particles can be understood as the result of a competition between orientational entropy and free volume entropy remains valid for the I–N transition in a system of hard plates. This was confirmed by the computer simulations of Veerman & Frenkel [51] (figure 3). In addition to the I–N transition, they observed a columnar phase in a system of hard cut spheres. In fact, the ratio of diameter to thickness has to be larger than 7 in order to observe the nematic phase; otherwise, there is a direct transition from the isotropic phase to the columnar phase. Furthermore, a very remarkable cubatic phase was reported by Veerman & Frenkel [51] in between the isotropic and the columnar phase. In this phase, the particles form small stacks of almost cube-like dimensions, which tend to align perpendicular to each other. However,
the thermodynamic stability of the cubic phase was questioned by Duncan et al. [52,53]. Recently, Marechal et al. [54] showed with computer simulations that the pressure at which the columnar phase becomes more stable than the isotropic phase is lower than the pressure at which long-range cubic order was found, which unambiguously shows that the cubic phase is thermodynamically unstable with respect to the columnar phase. The apparent stability of the cubic phase could be due to dynamic arrest. This is confirmed by experiments [55] that will be discussed below.

(ii) Selected systems of plate-like particles

Gibbsite. The mineral gibbsite (γ-Al(OH)₃) is an important intermediate in the Bayer process for aluminium production in the form of agglomerates of small crystals. Starting from the materials used in the Buining method [42] to produce boehmite rods, Wierenga et al. [56] discovered a synthesis route which yields well-formed hexagonal plate-like gibbsite crystals (diameter 100–200 nm and thickness 5–15 nm). Subsequently, van der Kooij & Lekkerkerker [57] succeeded in sterically stabilizing these gibbsite platelets by grafting a layer of low-molecular-weight PIB molecules onto their surface following the method of Buining & Lekkerkerker [36]. This novel model system of hard colloidal platelets was observed to phase-separate into an isotropic and a nematic LC phase [57]. Upon further increasing the particle concentration, van der Kooij et al. [58] observed that suspensions of these sterically stabilized plate-like gibbsite colloids also display a columnar phase (figure 4) in good agreement with the computer simulation results of Veerman & Frenkel [51].

In a suspension of charged gibbsite platelets, the particles interact through double-layer repulsions, which differentiates these particles from hard platelets. Not surprisingly, the LC phase behaviour now depends sensitively on the ionic strength [59–61]. By lowering the salt concentration and/or increasing the gibbsite concentration, the nematic phase gradually transforms from a discotic nematic (N₃D) into a columnar nematic (N₃C) phase with much stronger side-to-side interparticle correlations. Subsequently, this N₃C structure can be either transformed into the hexagonal columnar phase or arrested into a birefringent repulsive gel state with N₃C structure. Kleshchanok et al. [62] studied colloidal gibbsite platelets suspended in dimethyl sulphoxide (DMSO). They did not observe a nematic and a columnar phase but rather a layered LC phase consisting of hexagonally ordered particles, that is, an SmB phase. The use of DMSO, a polar aprotic solvent, leads to a long range of the electrostatic Coulomb repulsion between platelets, which the authors believe to be responsible for the formation of the SmB phase. Recently, high-quality computer simulations on systems of charged colloidal platelets have been reported [63], which support the transitions from a discotic nematic phase (N₃D), via a columnar nematic (N₃C) to a columnar phase (C). However, the SmB phase observed by Kleshchanok et al. [62] was not detected in these simulations.

Figure 4. Experimental phases for sterically stabilized gibbsite (I, isotropic; N, nematic; C, columnar) observed between crossed polarizers. Adapted from van der Kooij et al. [58]. © 2000, Macmillan Publishers Ltd. (Online version in colour.)
Nickel hydroxide

Brown et al. [64,65] prepared monodisperse plate-like particles of Ni(OH)₂ by controlled precipitation from dilute aqueous solutions of nickel(II) nitrate and ammonium hydroxide. These particles were sterically stabilized by adsorbing a sodium polyacrylate layer on the surface, providing particles that have short-range, repulsive interactions. They observed that these particles form a highly ordered phase when prepared as a concentrated dispersion, which was identified as a columnar phase using neutron scattering. Given the fact that the particles have an effective diameter of 103 nm and a thickness of 23 nm (hence \(D/L = 4.5\)), the observation that only a columnar phase is observed is in complete agreement with the computer simulation results of Veerman & Frenkel [51]. In 2010, Qazi et al. [55] put forward experimental evidence for the existence of cubic order in suspensions of these Ni(OH)₂ plate-like particles. Given the fact that computer simulations have shown unambiguously that the cubic phase is thermodynamically unstable with respect to the columnar phase, it seems reasonable to assume that the observed cubic phase is a dynamically arrested state.

Layered double hydroxides: hydrotalcite

The layered double hydroxide (LDH) platelets are particularly interesting, since they form an easy-to-synthesize class of colloidal, disc-shaped materials that can be adapted chemically to contain different metal ions and intercalated anions. The general formula for LDHs is \([\text{M}^{2+}]_{1-x}\text{[M}^{3+}]_{x}\text{(OH)}_{2}\text{[A}^{y-}]_{y}^{-}\text{mH}_{2}\text{O}\) with \(\text{M}^{2+}\) and \(\text{M}^{3+}\) different divalent and trivalent metal cations. LDHs are obtained by substituting part of the divalent cations by trivalent cations while the brucite-like structure is maintained. The possibility to introduce significant amounts of trivalent cations allows the LDH particles to have interesting tuneable optical and magnetic properties. Hydrotalcite is the LDH that contains Mg\(^{2+}\) and Al\(^{3+}\).

Colloidal platelets of hydrotalcite in the size range diameter 100–200 nm and thickness 10 nm have been prepared by co-precipitation of magnesium salts and aluminium salts [66–68]. By using different magnesium to aluminium ratios, one can tune the charge of the LDH particles. Liu et al. [69] and Wang et al. [70] observed that hydrotalcite suspensions with Mg/Al molar ratios 2:1 and 1:1 show different LC phase behaviour. The former shows a nematic phase [69] while, in the latter, a lamellar phase is observed [70]. As the net positive surface charge of Mg/Al LDHs comes from the replacement of a fraction of divalent Mg\(^{2+}\) ions by trivalent Al\(^{3+}\) ions, it can be presumed that the sample of (1:1) Mg/Al LDH has a charge density 1.5 times higher than that of (2:1) Mg/Al LDH. This is indeed reflected by a higher zeta potential (+43.6 mV versus +39 mV). Wang et al. [70] conjecture that the lamellar phase observed in (1:1) Mg/Al LDH suspensions arises from the stronger double-layer repulsion, although, in recent computer simulations on systems of charged colloidal platelets [63], the lamellar phase was not detected. Clearly, understanding this remarkable phase behaviour represents a challenging theoretical endeavour.

(c) Board/lath-like particles: theory, simulation and selected experimental systems

In the previous sections, we discussed systems in which two of the particle’s axes were (at least roughly) equally sized. If one allows three different dimensions (length \(L\), width \(W\) and thickness \(T\) with \(T < W < L\)) for the particle axes, additional LC phases are expected. This expectation is inspired by the prediction of so-called biaxial nematic (\(N_b\)) phases by Freiser in 1970 [71]. In this type of nematic phase, not only the most extreme axis of the particles is orientationally ordered, as in the usual (uniaxial) nematic \(N_u\) phases, but perpendicular to that also the two other axes have a preferred orientation. The search for such phases has turned out to be elusive for a long time, with the exception of the observation of a biaxial nematic phase in micellar systems [72] located in between two uniaxial phases of rod-like and disc-like micelles, respectively. However, it should be borne in mind that, in contrast to MCLCs, micelles are adaptive systems where particle shape and
phase symmetry mutually influence each other. Before we discuss potential examples of biaxial MCLCs, we briefly review what theory and simulations predict about typical size ratios for purely repulsive particles needed to observe a biaxial phase.

(i) Theory and computer simulation

Monte Carlo simulations on biaxial hard ellipsoids interpolating between rods and plates were performed by Camp & Allen [73] as shown in figure 5. They predict uniaxial rod-like and plate-like nematic phases bordering a rather small area of biaxial nematic exactly in the middle, when the variable width $W$ is close to the geometric mean of the other two dimensions,

$$W \approx \sqrt{LT} \text{ or equivalently } \frac{L}{W} \approx \frac{W}{T}. \quad (4.1)$$

A full phase diagram, including other (liquid) crystalline phases, was given by Taylor & Herzfeld [74] on the basis of scaled particle theory and cell models, where they found that the formation of a biaxial layer-like smectic ($SmA_B$) phase strongly competes with the $N_b$ phase, which only consists in a very small area (although incorporating length polydispersity could destabilize the smectic phase and might reduce this effect [75]).

(ii) Selected systems of board/lath-like particles

**Vanadium pentoxide.** A first potential experimental example is Zocher’s vanadium pentoxide—recently reviewed by Davidson [76]—which turns out to consist of long, thin ribbons of approximate thickness $T = 1 \text{ nm}$, width $W = 25 \text{ nm}$ and persistence length $L_p = 300 \text{ nm}$ (i.e. the length over which the ribbons are rigid and straight: their actual length may be much longer). From 0.5 to 0.7 per cent volume fraction dispersions display an isotropic–(uniaxial) nematic coexistence gap, which first extends into a true nematic phase but forms a nematic gel beyond 1.5 per cent volume fraction. Aligning particles within a modest shear field, a uniaxial alignment appeared persisting up to 4 per cent volume fraction, above which SAXS suddenly displayed patterns with biaxial nematic symmetry persisting for hours once the shear flow was stopped. This observation and a simultaneous change in the swelling behaviour could be indicative of a biaxial nematic phase, but the SAXS pattern might also be explained as induced by the shear and subsequently trapped in a gel state. Nevertheless, this system remains very alluring since...
a true biaxial nematic phase seems to underlie the gel state, especially when realizing that its dimensions closely approach the relationship $L_p/W \approx W/T$ (where the persistence length $L_p$ of these semiflexible ribbons takes the place of the total length $L$ in equation (4.1)).

Goethite

A true biaxial nematic mineral LC has been found [77,78] for goethite ($\alpha$-FeOOH). Under strongly basic conditions, goethite crystallites slowly grow and form approximately rectangular board-like particles (of length $L$, width $W$ and thickness $T$), which can subsequently be electrostatically stabilized at $\text{pH} = 3$. Depending on the details of the reaction and the subsequent centrifugation procedure, different (relative) sizes and polydispersities can be obtained. Samples of different volume fractions quickly performed an I-N phase separation, which through sedimentation and fractionation (continuing over months to years) formed clear isotropic, nematic [79] and smectic [80] phases (at polydispersities above 20% in combination with columnar phases [81]; figure 6).

One specific system of average dimensions $L \times W \times T = 254 \times 83 \times 28 \text{ nm}^3$ with typical polydispersities around 25 per cent was particularly close to the canonical relationship of equation (4.1). Microradian SAXS within the nematic phase revealed three strong liquid-like correlation peaks perpendicular to each other. The ratios between the correlation lengths corresponding to

Figure 6. Coexisting phases of polydisperse goethite: (a) sample between crossed polarizers, (b) SAXS and (c) schematic representation of the particles within the phases. (Online version in colour.)
these peaks closely agreed with the ratios between the average particle dimensions (especially when supplemented by the Debye length to take the soft repulsion between the double layers into account), providing conclusive evidence for a simple biaxial nematic phase [77]. At the lower osmotic pressures higher up in the sample, the biaxiality remained (although with slightly increasing correlation lengths, which is to be expected for a sedimented sample) without passing through a uniaxial nematic region before entering the isotropic phase. At first sight, this suggests that the sample is very close to passing through the bicritical point in the centre of figure 5, but it turns out that the polydispersity may play a significant role [82]. Also the smectic phase—displaying optical Bragg reflections—below the nematic phase was clearly biaxial. All reflections remain mutually perpendicular and are consistent with a biaxial smectic A phase. Batches of goethite with aspect ratios further away from relation (4.1) sometimes showed double correlation rings [78], but were never proved to be truly biaxial.

5. New frontiers

Over the last decade, the number of wet chemical synthesis routes providing high-aspect-ratio colloidal nanorods with interesting optical, electronic and catalytic properties has grown considerably (for reviews, see [83,84]). The challenge is to generate organized structures of these nanorods as they provide the basis for the engineering of new materials and the fabrication of devices. LC formation of nanorods provides in principle a simple and cost-efficient strategy for producing such structures (for a tutorial review of self-assembly of inorganic nanorods, see [85]). Before we highlight the difficulties and opportunities to master the self-assembly of this class of nanorods on the basis of a few representative examples, we illustrate some of the unique features MCLCs can display in external fields.

(a) Novel colloidal liquid crystal phases in external fields

Although low-molecular-weight LCs are commonly aligned and switched by applying external electric or magnetic fields, MCLCs are special in that individual particles can be highly susceptible to these fields. Since this already leads to orientational ordering of the particles within the originally isotropic (now called the paranematic) phase, the coexistence with the nematic phase shifts to lower volume fractions as predicted by Khokhlov & Semenov [86] and observed for rod-like TMV [87] and plate-like gibbsite [88] in magnetic fields. Depending on whether or not the easy axis of the particle coincides with its symmetry axis, the originally first-order I–N transition may vanish at a critical point or become second order [86].

As was discovered by Lemaire et al. [79,89], at colloidal dimensions, anti-ferromagnetic goethite displays very special magnetic properties. It aligns the long axis of its crystallites parallel to a low magnetic field (owing to a small uncompensated permanent magnetic moment along this axis) but their shortest axis parallel to a high magnetic field (the easy axis of magnetization being along the shortest axis). Depending on the particle size and the polydispersity, the transition from parallel to perpendicular alignment takes place around a magnetic field of 200–400 mT. This is accompanied by completely new phenomena such as a field-induced phase transition from a parallel nematic to a perpendicular columnar LC phase [90]. Furthermore, within an originally uniform nematic phase, a separation into two nematic phases can be induced by a magnetic field resulting in coexistence between a uniaxial nematic phase along the field and a biaxial nematic phase perpendicular to the field [91] (figure 7). The relative amounts turn out to depend on the field strength and polydispersity of the system.

For silica rods, the application of an external electric field leads to induced orientational order and the formation of nematic and smectic order at different volume fractions from those without an applied field (figure 2) and even a new C3-symmetric crystal structure owing to the interaction between the induced electric dipoles [49].
(b) Colloidal liquid crystals of mineral nanorods with special optical, electronic and catalytic properties

(i) Gold nanorods

Colloidal gold nanorods have received considerable attention in the last two decades because of their remarkable optical properties and potential applications (for a comprehensive review, including a historical perspective on colloidal gold dispersions, see [83]). The past two decades have witnessed rapid advances in the wet chemical synthesis of high-aspect-ratio cylindrical gold nanorods. Particularly interesting is the seed-mediated growth approach in the presence of surfactant [92]. Jana et al. [93] observed the formation of a nematic phase in concentrated suspensions of high-aspect-ratio gold nanorods. In addition to the nematic phase in suspension, nematic-like and smectic-like structures mediated by drying-induced self-assembly have been observed on a transmission electron microscopy (TEM) grid [83,94]. Remarkably, for long nanorods (of aspect ratio = 6 (figure 8)) isotropic, nematic-like and smectic-like assemblies have been observed in this way, while for short (aspect ratio = 3) nanorods the nematic-like assemblies were absent. This observation is highly reminiscent of the aspect-ratio-dependent phase behaviour of rods observed in suspension (see §4a(i)) and suggests that the LC structures observed after drying on a TEM grid are formed in the precursor suspension. To prove this unequivocally, the challenge remains to observe them in situ.

It has long been known that the colour of colloidal dispersions of gold particles varies from red to blue, depending upon the size and shape of the particles [83]. Potential applications of LCs of colloidal gold nanorods lie in their remarkable optical properties originating from two distinct surface plasmon resonance (SPR) absorption bands of individual rods. The transverse SPR absorption band—due to the excitation across the short dimension of the rods—is relatively insensitive to the rod aspect ratio and coincides spectrally with the SPR absorption around 520 nm of spherical nanoparticles (origin of their reddish colour). In contrast, the longitudinal SPR band—associated with the excitation along the long axis of the rods—is greatly red shifted and very sensitive to the aspect ratio.

Caseri [95] made clever use of these dichroic properties by stretching a PVA/gold sphere nanocomposite film. The spherical gold nanoparticles can form ‘pearl necklace type arrays’ by aggregating along the stretching direction. Placing this nanocomposite film in an optical device...
with switchable polarization direction (a twisted nematic cell), he could produce a bicoloured display. While interesting, this device is clearly a long way from the ideal of a switchable gold rod nematic LC.

(ii) CdSe and CdSe/CdS nanorods

Like colloidal gold nanorods, both CdSe and CdSe/CdS semiconductor nanorods have received considerable attention in the last two decades; in the latter case, because of their remarkable photoluminescence properties. Colloidal CdSe and CdSe/CdS semiconductor nanorods have the interesting property that they exhibit linearly polarized emission perpendicular to the long axis [96]. Moreover, CdSe/CdS heteronanorods present the appealing characteristics of strong and tunable light emission from green to red depending on the ratio between the CdS rod diameter and the CdSe nuclear diameter [97]. The ability to control the shape of CdSe and CdSe/CdS semiconductors has grown dramatically in recent years (for a critical review of the synthesis methods of semiconductor nanoparticles, see [84]). Peng et al. [98] demonstrated that by controlling the growth kinetics the shapes of the resulting cadmium selenide nanoparticles can be tuned to vary from a nearly spherical morphology to a rod-like one, with aspect ratios as large as 10 to 1. Li et al. [99,100] observed the formation of a nematic LC phase in suspensions of these CdSe semiconductor nanorods. Smectic-like LC structures mediated by drying-induced self-assembly on a TEM grid were observed for CdSe nanorods by Li & Alivisatos [101] and for CdSe/CdS heteronanorods by Carbone et al. [97], while Talapin et al. [102] took the drying-induced self-assembly method one step further to produce highly luminescent smectic three-dimensional structures of CdSe and CdSe/CdS.

More recently, Baranov et al. [103] succeeded in producing two-dimensional smectic monolayers of close-packed hexagonally ordered arrays of nanorods directly in solution by tuning the depletion attraction forces between CdSe/CdS nanorods with surfactant micelles as illustrated in figure 9.

The origin of the depletion attraction lies in the unbalanced osmotic pressure between two colloidal particles when the depletion layers of the added (non-absorbing) species around the colloidal particles overlap. This mechanism was first put forward by Asakura & Oosawa [104] on the basis of a simple statistical mechanical theory (for an overview of the depletion interaction in colloidal suspensions see [105]). Clearly, the assembly of colloidal nanorods in solution by the depletion attraction has the potential to enable fabrication procedures for materials based on self-organized colloidal structures.

(iii) TiO2 rutile nanorods

A nice example of the potential of LC nanorods for catalytic purposes was given by Dessombz et al. [106], who synthesized rutile (TiO2) nanorods of average length 160 nm and average diameter 15 nm that displayed an I–N phase separation in aqueous solution. These LC
Figure 9. Illustration of the formation of two-dimensional smectic monolayers using the depletion attraction induced by added surfactant micelles (see text). Adapted from Baranov et al. [103]. © 2010, American Chemical Society. (Online version in colour.)

suspensions could be spin-coated into well-aligned rutile films, the photocatalytic properties of which were examined by monitoring the decomposition of methylene blue under UV light. It was demonstrated that UV light polarized along the quadratic axis of the rutile nanorods was most efficient for this photocatalytic reaction.

6. Synopsis and outlook

Looking back upon the preceding sections, we may conclude that, almost a century after their discovery, MCLCs remain a vibrant field of research with a distinguished past and an exciting future.

Although after 70 years Onsager’s explanation of the formation of a nematic phase—a decrease in excluded volume compensating for a loss of orientational entropy—remains unassailed, its extension by computer simulations has considerably widened the scope of the Onsager argument, including more highly ordered LC phases which have been observed in suspensions of anisometric mineral colloids. While the entropy-driven self-organization of anisometric colloids is determined by their shape, it was observed that by tuning the long-range repulsion LC phases are observed (lamellar and SmB phases) which so far have not been predicted by theory or simulation and still present a challenge.

In the last decade, the potential of wet chemical synthesis routes to provide high-aspect-ratio colloidal nanorods with interesting directional, optical, electronic and catalytic properties has grown drastically. Through innovative and ingenious approaches, significant progress has been made in arranging these anisotropic nanoparticles into ordered assemblies. While LC formation of nanorods in principle provides a simple and cost-efficient strategy for producing such structures and some promising steps have been made (such as the use of the depletion interaction), clearly the field is still in its infancy leaving significant opportunities for future developments, where also the unique behaviour of mineral LCs in external fields can play an important role.
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References


