Confinement effects on lyotropic nematic liquid crystal phases of graphene oxide dispersions

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Abstract

Graphene oxide (GO) forms well ordered liquid crystal (LC) phases in polar solvents. Here, we map the lyotropic phase diagram of GO as a function of the lateral dimensions of the GO flakes, their concentration, geometrical confinement configuration and solvent polarity. GO flakes were prepared in water and transferred into other polar solvents. Polarising optical microscopy (POM) was used to determine the phase evolution through the isotropic-biphasic-nematic transitions of the GO LC. We report that the confinement volume and geometry relative to the particle size is critical for the observation of the lyotropic phase, specifically, this determines the low-end concentration limit for the detection of the GO LC. Additionally, a solvent with higher polarisability stabilises the LC phases at lower concentrations and smaller flake sizes. GO LCs have been proposed for a range of applications from display technologies to conductive fibres, and the behaviour of LC phase formation under confinement imposes a limit on miniaturisation of the dimensions of such GO LC systems which could significantly impact on their potential applications.

1. Introduction

Graphene oxide (GO) has garnered significant attention in recent years as a derivative of graphene which shows significant mechanical strength and chemical versatility while being produced and processed in large quantities, specifically for mechanical reinforcement in nano-composites, as a source of reduced GO for electrical and thermal applications, and as an optical material [1, 2]. GO is known to form highly stable colloidal liquid crystalline phases in aqueous and a variety of organic polar solvents, which is essential for some of GO’s most promising applications such as wet-spun fibres and GO liquid crystal displays [3–14].

Liquid crystals (LC), in general, are characterised by their fluidity combined with ordering that results in directional and anisotropic properties common to crystalline systems [15–17]. The LC phase may be formed when the material is made up of shape-anisotropic (rod or disc-like) molecules or anisotropic (non-spherical) particles. When the liquid crystalline state is achieved purely by temperature variation, then the phase is called thermotropic. When colloids of anisotropic particles form LC phases within a particular concentration and temperature range, they are said to be lyotropic [18]. In general, the colloidal suspensions of geometrically anisotropic particles can produce a LC phase above a critical concentration. The critical volume fraction \( V_{\text{crit}} \) depends on the aspect ratio, \( A_R = W/L \), of the particle as \( V_{\text{crit}} \approx 4/AR = 4L/W \) [19], where for 2D particles, \( L \) and \( W \) represent the thickness and the lateral width.

The liquid crystalline behaviour of anisotropic colloids was first observed in the tobacco and tomato mosaic virus (TMV) [20] and vanadium pentoxide (\( \text{V}_2\text{O}_5 \)) [21] in the early 20th century. A few decades later Mourchid et al. studied colloidal plate-like charged particles and clay particles to report liquid crystalline behaviour [22]. They found that the concentration and the ionic properties of the particles are crucial for controlling the stability of the suspension. The first theoretical work was reported by Onsager [19]. The theory of Onsager was based on the fact that when the concentration of particles reaches a certain level, the freedom of the particles is constrained. As a result, the entropy of the colloid decreases due to overlapping excluded volumes of the particles.
To compensate the entropy decrease, the particles start to acquire orientational order. Thus, above a critical concentration orientation order is achieved and a nematic LC phase is formed. Similarly colloidal suspensions of 1 dimensional (1D) carbon nanotubes (CNTs) have shown a phase transition to the nematic LC phase [23–25]. In CNT LCs, the order parameter, which is a measure of the degree of order of the LC phase, can be modified by controlling their length and entanglement [26].

The corresponding 2 dimensional (2D) nanoparticle is graphene, and it’s derivative GO which is decorated with a variety of oxygen-containing functional groups such as carboxyl, hydroxyl and epoxide on its basal plane and edges [8, 27]. GO retains a significant fraction of the mechanical strength of pristine graphene, is chemically versatile to a wide range of organic chemistry reactions due to the abundance of reactive functional groups, and can be exfoliated from graphite into monolayer particles that possess a large aspect ratio greater than $10^4$. The oxygen-containing functional groups distinguish GO from graphene in allowing for a high dispersibility in water and other polar solvents.

GO dispersions in polar solvents, especially water, are known to exhibit highly stable lyotropic nematic phases at fairly low concentrations, especially for particles of high aspect ratio. Such dispersions have been employed as a starting point for wet-spinning of GO fibres which display extraordinary strength and flexibility, and when converted to reduced (r)GO, also display high electrical conductivity [28]. GO LCs have also been demonstrated for LC display and other optical applications [4, 5], and to produce conductive transparent electrodes to replace indium tin oxide in the display industry [29, 30]. In all such applications, there is either a processing step or application design incumbent to study the effect of confinement on the properties on the resulting material. It is therefore essential to understand the formation, stability and observability of the GO LC phase as function of other parameters such as particle size and concentration.

In this study, GO LC samples with mean particle sizes from 0.5 to 20 µm and concentration from 0.5 to 4 mg ml$^{-1}$ were studied within geometries of 50 to 500 µm thickness. In addition, the dependence of the lyotropic nematic phase on the GO-concentration in different solvents is examined, specifically deionised water (DIW), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The interplay between cell thickness, flake concentration, flake size, isotropic solvent and temperature on LC phase stability was investigated and the regions of stable LC phase, biphasic and isotropic or pseudo-isotropic phases was mapped.

2. Materials and methods

2.1. Sample preparation

GO was prepared from graphite flakes in DI water by a modified Hummers’ method [31, 32] and then redispersed into two other solvents, DMF and DMSO. Briefly, graphite (10 g, 80 mesh, 94% C) was first treated with NaNO$_3$ (9 g, Sigma-Aldrich) and concentrated H$_2$SO$_4$ (338 ml, Sigma-Aldrich) at room temperature (RT) for 3 h to obtain intercalated graphite. The mixture was cooled in an ice bath and 45 g of KMnO$_4$ (Sigma-Aldrich) were gradually added. After addition of the oxidizing agent, the reaction mixture was stirred at RT for 1 week to complete the oxidation. The oxidised graphite slurry was then diluted with a solution of 5% H$_2$SO$_4$, followed by the slow addition of 5 g of H$_2$O$_2$ (Sigma-Aldrich) as a solution. The resulting graphite oxide was purified by repeated centrifugation and redispersion in DI water until the pH of the supernatant was neutral. Appropriate amounts of GO were dried, weighed and redispersed in DI water, DMF and DMSO to obtain a concentration of 4 mg ml$^{-1}$. To avoid the flake damage, the dispersions were made by stirring the GO powder for 1 week with the magnetic stirrer, followed by 10 min of high shear mixing at 6000 RPM with a Silverson Model L4M shear mixer. This process ensures that the GO concentration is solely determined by the initial mass of dry GO and the solvent volume; there is no loss of GO material during redispersion or other factors that might affect concentration. The other concentrations were made by diluting the stock dispersion. GO dispersions of different size distributions were prepared by starting with a dispersion of large mean flake size and subjecting it to different durations of shear or ultrasonic mixing, namely shear mixing for 1, 2, 5 h respectively using 8000 rpm for the first 3 sizes, and ultrasonication (100% power, 37 kHz) for 2 h for the smaller size.

For the sake of convenience, we can approximate the density of GO to that of the parent material graphite at 2266 mg cm$^{-3}$, which allows for an interconversion of 1.0 mg ml$^{-1}$ to 0.102 wt.% to 0.044 vol.% of GO in aqueous suspension.

Microscopy slide glasses of 2.5 cm $\times$ 2.5 cm were cut and washed in acetone and methanol in a sonication bath for 30 min. To study the LC properties by means of POM, sandwich cells were assembled with different gaps of 50, 100, 150, etc up to 500 µm controlled by spacers and glued using a UV curable glue (Norland N68) as shown in figure 3(a). The cells were filled by capillary action with the dispersions of different GO concentrations.

2.2. Characterisation

Scanning electron microscopy (SEM) was performed on a Zeiss Ultra SEM. UV–vis spectroscopy was carried out in a Genesys 10S spectrophotometer. Texture image acquisition was performed by means of a Leica DMLP polarising microscope and a uEye digital
camera at resolution 2048 × 1088 pixels. The sample temperature was controlled by a Linkam TMS94 hot-stage and temperature controller, with relative accuracy of ±0.1 K. The zeta-potential measurements were carried out by using a Malvern Zetasizer Nano Z apparatus. The mass loss upon heating and reducing the GO to rGO was examined via thermogravimetric analysis (TGA, Q5000 from TA Instruments). Phase transition studies were carried out using differential scanning calorimetry (DSC, Perkin Elmer Diamond).

3. Results and discussion

3.1. Optical absorption and dispersion colour

As shown in figure 1(a), the samples are named as GO-DIW, GO-DMSO, and GO-DMF respectively. We note that the GO-DIW solutions appear lighter than those of the other samples, when in fact the concentrations are identical. The fact that different GO dispersions of the same concentration in different solvents have different colour has been previously reported [33–35]. This colour variation was correlated to UV–vis absorption spectroscopy on the three GO dispersions at concentration of 0.02 mg ml⁻¹ (figure 1(b)), which indicates that GO dispersed in DMF and DMSO have higher absorption intensities compared to the GO in DIW, whereas the shape of the spectra in the visible region is similar, so more accurately, there is a difference in colour intensity rather than colour itself, between the three dispersions. The mechanism behind this colour difference is still under investigation. Pendolino et al attributed a difference in the colour of GO dispersions in water and methanol to structural modifications when dispersed in different polar solvents [36]. Results of UV–vis spectra and visual inspection could be interpreted as chemical modification of GO dispersed in DMF and DMSO, considering the fact that an increased absorption intensity is an indication of the extension of π−π* conjugated domains which occurs during the reduction/deoxygenation of GO. In that case a red shift of π−π* (230 nm) transition peak will occur. Unfortunately, from our measurements we cannot observe the 230 nm peaks of GO in DMF and DMSO because the residual solvents absorption peaks in the same region. On the other hand, we consider the significant structural differences regarding the water and DMF/DMSO as solvents; water is polar protic while DMF and DMSO are aprotic respectively, they exhibit different relative static permittivities (often referred to as dielectric constant), and different hydrogen bonding abilities. We speculate that the mechanism of stabilisation between GO-DIW and GO-DMF/DMSO is different. Whereas in water the GO is stabilised by hydrogen bonds formed with the water molecules (proton solvent) and electrostatic repulsion between GO flakes because of the negatively charged carboxylate groups, in DMF and DMSO (aprotic solvents) the mechanism of stabilisation can be rather attributed to a layer of confined solvent near the surface which prevent aggregation via steric. This results in a different solvent molecule density at the vicinity of the GO flakes compared to the bulk solvent volume, resulting in a change in the local refractive index (RI), even though the bulk RI of the three solvents are similar. This in turn would result in higher absorption intensities, and consequently darker colour. A detailed study of this phenomenon is beyond the scope of this paper but it suffices to note here that the dispersion concentrations are accurate and different interaction mechanisms between the GO flakes and solvents are responsible for the observed colour variations.

3.2. Size distribution of GO dispersions

The size distribution of all GO dispersions were characterised using SEM (figure 2). The sizes of 200 flakes from multiple SEM images for each suspension was measured manually using ImageJ®, always in the horizontal direction through the centre of the flake in order that shape anisotropies do not skew the distribution results; it is assumed that the drying process does not introduce any orientation anisotropy. A typical feature of the exfoliation process, and also due to the irregularity and various polygonal shapes of the GO flakes, the size distributions are relatively broad for all four GO samples as shown in the inset of figure 2. The size distribution is affected by the particle and grain size in the starting graphite material, the intercalation, oxidation and exfoliation conditions in the preparation of GO, and the subsequent redispersion and size reduction efforts that involve shear or ultrasonic mixing. All these processes tend to yield broad size distributions. Nonetheless, the dispersions we have selected have statistically significant differences in their size distributions.

3.3. Colloidal stability and choice of solvents

The zeta (ζ)-potential is a widely accepted significant indicator of the stability and sedimentation behavior of colloidal dispersions. The magnitude of the ζ-potential demonstrates the level of electrostatic repulsion between charged particles in the dispersant medium. When the ζ-potential is small, attractive forces may overcome the repulsive forces, the dispersion will destabilise and the particles aggregate. However, high ζ potential (negative or positive) confirms the stability of colloidal suspensions and their resistance to aggregation [37, 38]. The stability of diluted GO-DIW were examined by the ζ-potential technique, yielding ζ-potential of −46 mV at a concentration of 0.02 mg ml⁻¹, which is more negative than that of standard stable colloids. The values are an indication of the excellent dispersion of GO in water [4].

The choice of other solvents for this work was based on a set of criteria specific to lyotropic phase formation and study. The solvents should be capable of dispersing
GO stably at high concentration, without aggregation, and without the need for ultrasonication which will affect the flake size. Furthermore, the solvent should be high-boiling to prevent evaporation and variation of concentration over the course of the experiment. This rules out solvents like N-methylpyrrolidone (NMP) and N-cyclohexyl-2-pyrrolidone (CHP) which requires ultrasonication for complete dispersion, and

![Figure 1](image1.png)

**Figure 1.** (a) Photographs of the GO suspensions GO-DIW, GO-DMSO, and GO-DMF of different concentration ranges from 0.5 to 4.0 mg ml$^{-1}$ as labelled. The concentration increase clearly manifests itself by a darkening of the suspension. It can also be seen that the suspensions are stable, and no agglomeration is observed. (b) UV–vis absorption spectra of GO suspensions GO-DIW, GO-DMSO, and GO-DMF at 0.02 mg ml$^{-1}$ concentration after subtraction of the solvent absorption background.

![Figure 2](image2.png)

**Figure 2.** Four different average sizes of GO flakes were produced and characterized by SEM (insets, note the difference in scale); these were (a) 16.8 ± 10.1 µm, (b) 7.4 ± 4.7 µm, (c) 4.6 ± 4.1 µm and (d) 0.27 ± 0.16 µm. The solid lines are fits of the histograms with a log-normal distribution and are a guide to the eye.
low-boiling solvents such as acetone and tetrahydrofuran (THF). DMF and DMSO adhere to the criteria outlined here, while providing significant variation in relative static permittivity to water, and were therefore selected for this study.

3.4. Effect of boundary conditions

LCs in general are strongly influenced by the boundary conditions of the substrates, confinement and anchoring as a result of the interaction between the LC molecules and the bounding surfaces [39]. A variety of polymer layers, spin coated and rubbed are employed to promote alignment of thermotropic LC phases [39, 40]. However, for the systems investigated here, none of these procedures have provided any particular alignment as commonly observed for thermotropic LCs. As can be seen in figure 3, polarizing microscopy reveals that alignment of the GO lyotropic nematic can also be obtained without any surface modification to the glass surfaces, as the substrates used were only cleaned, but not treated for any particular alignment. Uniform birefringence indicates a homogeneous alignment of the director \( \mathbf{N} \) throughout the cell and over large length scales, i.e. the GO plane is parallel to the bounding glass plates. Here the suspensions were examined in two geometries; (i) the cell bounded on the sides by spacers with a glass coverslip covering the top and bottom of the cell, producing a ‘closed channel’ and (ii) a similar cell but without a top glass coverslip, producing an ‘open channel’ geometry respectively. The texture of cell (i) is shown in figure 3(b), along with the schematic side-view diagram of the cell including the GO flake orientation, figure 3(c). In the case of GO flakes, the director \( \mathbf{N} \), i.e. the most common axis of orientation, is defined as the normal to the flake, thus perpendicular to the plane of the flake, and indicated by arrows in the figure. The central part of the cell shows a dark phase appearance with zero birefringence (light propagation parallel to the optic axis), known as the homeotropic or pseudo-isotropic orientation as it mimics the lack of birefringence observed in the isotropic phase. The birefringence becomes pronounced towards the edges of the cell. A splay of the GO flakes, thus a bend of the director, is observed as we move from the bounding glass plate towards the middle of the cell, changing the transmitted light intensity from bright to dark. The opposite scenario is observed moving further to the opposite bounding plate, exhibiting a symmetric pattern from dark to bright. This suggests that when GO is bound by parallel surfaces, owing partly to the strong interaction between the hydrophilic GO and glass surfaces, the flakes align parallel to the bounding surfaces.

However, in cell (ii) without the glass cover, figures 3(d) and (e), the birefringent area is visible throughout the whole cell, the transmitted intensity only slightly reduced in the middle of the cell, due to the slight splay of the GO flakes caused by the curvature of the LC-air interface. In this configuration the director \( \mathbf{N} \) follows the curvature of the free top surface. The POM texture can be attributed to the GO alignments schematically depicted in figure 3(e). The direction of the flakes with respect to glass has been investigated previously [10], where it was proposed that the observed alignment relative to the top and bottom sides of the cell is likely to be metastable since it is partially triggered by the assembling kinetics during the cell preparation by capillary action, and also by the elasticity of the LC phase. In contrast, we found that the homogeneous, well aligned texture can be retained for days as long as the cell is completely sealed and no solvent evaporates. Both geometries point to the strong, planar anchoring between GO flakes and the glass surface.

The direction of the alignment has been further investigated by rotating the sample in the channel geometry between crossed polarizers. As shown in figure 4, by rotating the cell along the viewing axis perpendicular to the viewing direction, the bright and the dark states are reached with a periodicity of 90°. This indicates a well-aligned director of the liquid crystalline phase of GO colloids, with lowest transmission at 0° and 90° and maximum transmission at 45°.

Figures 5(a)–(c) show GO textures of the lyotropic nematic phase in GO suspensions for different solvents as a function of concentration and sample thickness. Since the birefringence of the lyotropic nematic LC phase is of the order of \( 10^{-3} \) [18], the thickness of the samples has to be markedly larger compared to the samples prepared for thermotropic LC phases [41, 42]. Here the range of the thickness of the sandwich cells is \( d = 50–500 \ \mu m \), and the range of the LC concentrations is \( c = 0.5–4.0 \ \text{mg} \ \text{ml}^{-1} \) for all solvents (DIW, DMSO and DMF). For all three solvents it is seen that the nematic lyotropic phase can not be observed for low GO concentrations or narrow cell gaps. This could be due to two reasons: (i) the birefringence is suppressed by homeotropic or pseudo-isotropic alignment, or (ii) the LC phase is altogether suppressed by thin cell gaps, leading to the formation of an isotropic phase, at small cell gaps and low concentrations. The macroscopic appearance of the two scenarios is nearly indistinguishable.

However, the total suppression of the nematic phase due to narrow cells gaps is counterintuitive, rather, one would expect the opposite behaviour based on the strong anchoring and planar alignment of GO flakes at the glass surface as seen in figure 3.

On the other hand, it should be noted that for thermotropic LCs, the application of mechanical shear or a magnetic field can generally be used to at least temporarily reorient the director from pseudo-isotropic, homeotropic orientation to a birefringent, planar one. This leads to a temporary tilt of the molecules and thus to birefringence, which can be observed as a bright flash in polarizing microscopy. A respective effect will not be observable for a true isotropic phase. For
GO LCs, the application of mechanical shear caused no birefringence which would be detected as flash of transmitted light. Secondly, the application of a magnetic field \([43, 44]\) at a strength of 0.2 T at an angle of \(~80°\) to the director (in situ under the microscope) does not induce reorientation and planar alignment either.

The uncharacteristic lack of response to shear and magnetic fields could also be attributed to the strong anchoring of the GO flakes by the bounding glass surfaces, and the consequently imposed ordering that propagates the whole cell, the effect of which is particularly stronger for thinner cell gaps. We therefore favour the first interpretation, that the confinement imposed here results in the formation of homeotropic alignment and pseudo-isotropic behaviour, reinforced by the strong anchoring of the GO flakes between parallel glass surfaces.

It should further be pointed out that the observed behaviour is independent of solvent. The pseudoisotropic phase, observed at low concentration or small gaps, transforms into a biphasic region characterised by partial birefringence at moderate concentrations or gaps, after which the lyotropic nematic phase eventually fully develops and is observable even for small cell gaps at high-enough concentrations, or at low concentrations for large-enough gaps. From the texture grids it can clearly be seen that the phase formation is most easily achieved for DIW, as compared to DMSO and

**Figure 3.** (a) Schematic of LC cell comprised of two glass slides separated by a spacer forming a channel which is filled with the GO LC. (b) and (d) Optical microscope image in top view (B) of the cell of thickness 1.1 mm with GO-DIW (1.5 mg ml\(^{-1}\)), (b) with a cover slip (closed channel), where the central dark area has a director \(\mathbf{n}\) which is perpendicular to the plane of the image, while the edges are in the plane of the image and (c) without a cover slip (open channel), when the director follows the direction of the natural curvature of the surface. The schematic diagrams of flake alignment corresponding to the images in both cases are shown in (d) and (e) respectively, in cross-sectional side view (A) of the cell.

**Figure 4.** POM images of GO-DIW (1.5 mg ml\(^{-1}\)) of a cell without coverslip, showing the alignment of the liquid crystalline phase as the cell is rotated through 4 angles, (a) 45°, (b) 60°, (c) 75°, and (d) 90°. The bright and the dark states occur with a periodicity of 90°. The dark region on either side of the band of GO LC is the cell walls.
DMF, both of which are aprotic, and have a relative static permittivity of approximately half that of DIW (DIW: \(\varepsilon' = 88\), DMSO: \(\varepsilon' = 46\) and DMF: \(\varepsilon' = 36\)).

Figures 5(d)–(f) shows the transmitted light intensity through the samples where their photographs are shown in figures 5(a)–(c) respectively. GO-DIW shows a smooth trend with regards to both the concentrations and the thickness of the sample. While for the other solvents, the transmitted intensity fluctuates somewhat with respect to sample thicknesses, most likely due to director misalignment. The measurements indicate that the onset of liquid crystalline phase observation for GO-DIW is occurring at lower sample thicknesses for equal concentrations as compared to GO-DMSO and GO-DMF. Or from a different perspective, at a comparable sample thickness the nematic phase of GO-DIW is better developed than for the other two solvents. Again, we believe that this is due to better phase formation either due to the protic nature or higher relative static permittivity of water.

3.5. Effect of GO flake size

The size or the aspect ratio of the GO flakes plays an essential role in the formation of the lyotropic phase [11]. There is a limit for the particle size of the sample to yield an observable lyotropic nematic phase. It is known that below GO flakes of very small size do not order to produce a LC phase and are instead isotropically oriented. Figure 6 shows the dependence of the lyotropic nematic phase on the size of the GO flakes as a function of gap size. When confinement is
imposed, the isotropic appearance, in the form of the pseudo-isotropic phase, extends even to higher GO flake sizes for the smaller gap sizes. The transitions between the pseudo-isotropic to biphasic to nematic states are clearly seen for all flake sizes larger than 0.27 \( \mu \text{m} \). In another view, the lyotropic liquid crystalline phase formation in favour of pseudo-isotropic behaviour is enhanced for increasing GO flake size for any given gap.

### 3.6. Nematic to isotropic phase transition

So far, it has been shown that the transition from a pseudo-isotropic to a lyotropic nematic phase state \( T_{N-I} \) depends on the size of the GO flakes, their concentration, thickness of the sample and the polarity of the solvent. Additionally, both temperature and concentration dependence can be incorporated into the phase diagram for describing the lyotropic nematic of GO suspensions.

Figure 7(a) shows the temperature stability of the LC phases by POM while the sample was being heated. This did not reveal any transition to an isotropic phase in the temperature region starting from RT to the vicinity of the boiling point of the solvent or maximum accessible temperature with the LC test cells before destruction. The TGA scan, figure 7(b), of GO clearly shows that there is a mass loss upon heating. Some of the mass-loss in the temperature range of 25–165 °C can be attributed to the water loss, CO and CO\(_2\) [45], despite having dried the GO previously. The chemical transition of GO to rGO occurs at approximately \( T = 165 \) °C (see figure 7(b)), a temperature which was also observed by Cui et al [45] for this process. Above 165 °C, the hydrophobic nature of rGO dominates dispersion stability and results in flocculation or aggregation, and consequently rGO does not form LC phases in aqueous media [26]. Thus TGA has revealed that the GO employed in our investigations is chemically stable from RT up to approximately 165 °C.

Secondly, DSC was used to possibly reveal any thermodynamic changes. As shown in figure 7(c), two samples (GO-DIW) with concentrations 1.1 and 0.55 mg ml\(^{-1}\) were investigated. The results of DSC, similar to POM, did not show any phase transition up
to 60 °C. To avoid contaminating the DSC system, the maximum temperature of 60 °C was chosen, because of the solvent, the sample pans have to be heated with a hole in the lid, allowing evaporation at increased temperatures. Similarly, Kim et al have reported that the nematic phase was maintained up to the boiling point of the solvent [11]. It can thus be concluded that once the lyotropic phase has been formed, it is very stable. In contrast to common lyotropic phases [18], the mesogenic units of GO LC are solid flakes with a 2D carbon backbone with functional groups and not produced by weak bonding of small amphiphilic molecules for instance, energies of the order of $kT$ are not likely to break bonds easily upon heating to a temperature $T$, where $k$ is the Boltzmann constant.

It has been demonstrated that graphene LCs can be used in displays based on Kerr effect [4] which would have the advantage of fast switching and no viewing angle compensation considerations. Additionally, GO LCs is the starting material for wet-spun graphene fibres [46] which have potential applications in smart textiles and sensors. Lastly, GO and its derivatives encounter a number of confinement and flow conditions during their production, processing and applications such as ink-jet printing [47], which will all be impacted by the confinement effects reported here.

4. Conclusions

Stable dispersions of GO in DI water and other solvents were prepared at a range of particle sizes and concentrations. The GO suspensions exhibited a lyotropic nematic LC phase that is dependent on a variety of parameters. Firstly, liquid crystalline behaviour is more pronounced for increasing concentration and especially also for increasing size of the GO flakes. Our investigations indicate that for small cell gaps the birefringence is suppressed and can thus not be observed by polarising microscopy. This is attributed to the formation of a strongly anchored homeotropic alignment of the GO flakes leading to a pseudo-isotropic behaviour in favour of the birefringent lyotrophic nematic phase. It is also observed that the solvent medium plays an important role in the formation of the lyotropic nematic phase; in water which is a protic solvent with higher relative static permittivity, the nematic phase forms at lower GO concentrations and at smaller flake sizes. Confinement conditions and GO-substrate interactions have a pronounced effect on the orientation of the lyotrophic nematic director even for untreated substrates. The confinement effect we report is valid across different solvents with different degrees of lyotropic phase stability. These confinement effects should be taken into consideration when designing processes and products that employ GO LC phases. Employing several methods, such as POM and DSC, we could not detect any phase changes to an isotropic phase simply on heating the samples up to the boiling point of the solvent.

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