A small-angle X-ray scattering study of nanoparticle assembly in an aligned nematic liquid crystal

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The assembly of colloidal particles in a nematic liquid crystal has been investigated using small-angle X-ray scattering. The structure and orientation of nanoparticle assemblies in bulk samples of aligned nematic liquid crystal have been determined. The method offers some advantages over optical microscopy, which is usually restricted to investigations of thin cells and micron-sized particles. The scattering from chains of particles has been calculated, and comparison with experimental results has shown that suspensions of 48 and 105 nm diameter silica nanoparticles formed highly ordered structures perpendicular to the liquid crystal director, consistent with quadrupolar defect-induced assembly.

Keywords: small-angle X-ray scattering; alignment; defects; liquid crystal; nanoparticles

1. Introduction

There is currently a strong drive to utilise the combined properties of nanoparticles and liquid crystals [1] in topics as diverse as carbon nanotube dispersion, [2,3] chemical and biological sensors [4] and components for microphotonics.[5] There is also considerable interest in using nanoparticle-doped liquid crystals in more conventional liquid crystal display applications, where nanoparticle-induced properties have breathed new life into old display materials. Nanoparticle doping has been used to improve the bulk properties of liquid crystals through reducing their operating voltages and response times,[6,7] or to incorporate increased functionality in display devices. Examples include induced bistability through screening of electrode surfaces by a nanoparticle cloud [8] and direct incorporation of a tuneable colour response through plasmonic nanoparticle arrays. [9] Nevertheless, while many of the desirable properties of liquid crystal–particle composites manifest as a change in a bulk property, on a single particle level, the interactions between embedded particles are remarkably complex, and a better understanding of their long-term stability is particularly important as nanoparticle-doped devices become more feasible.

In a typical antiparallel rubbed cell, the liquid crystal director is uniform, while at a N,N-didecyl-N-methyl-(3-trimethoxysilylpropyl)ammonium chloride-, octadecyl trichlorosilane-[10] or dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DMOAP)-[11] modified particle surface, the liquid crystal anchors radially. This homeotropic anchoring is not compatible with the background liquid crystal director, and so when a particle is embedded in an aligned liquid crystal, a defect is formed. The type of defect can be varied with more complex surface treatments,[12] but typically, the defect is either a dipole or a quadrupole and can be clearly observed using polarising optical microscopy. It is favourable for the particles to assemble to minimise the elastic distortion of the nematic director field. The assembled structures are generally chain-like in nature and oriented parallel to the director for dipole defects and perpendicular to the director for quadrupoles. Micron-sized particles normally generate quadrupolar defects, but there is a critical diameter,[13] typically a few microns, dependent on the surface quadrupolar anchoring strength of the particle and the elastic properties of the liquid crystal,[14] where the quadrupolar defect configuration becomes less favourable and so larger particles tend to generate dipolar defects. Additionally, by decreasing the cell thickness to a few microns,[15] dipolar defects can be transformed into quadrupolar defects. Furthermore, by using optical tweezers, particles at the size threshold between the two defect regimes can be both manipulated [16] and switched between defect configurations. This is done by locally heating the liquid crystal to the isotropic phase using the trapping laser, and allowing to cool back to the nematic phase.[17] Due to the anisotropic interaction potential around such defects, microparticles can be assembled into complex and stable one-, [18] two- [19] and three-dimensional structures [20] with potential novel electro-optical response.[21]
While this approach is ideal for particles with sizes in excess of 1 micron, many useful properties are manifest by much smaller nanoparticles, for which these techniques are not suitable.

Koenig et al. [22,23] first demonstrated that the binding energy between 169 nm diameter gold nanoparticles dispersed in an aligned cell of nematic liquid crystal could be measured using video-tracking dark-field microscopy and observed the reversible formation of particle dimers with binding energy \( < 5k_B T \). It is widely accepted that for particles smaller than a critical diameter (approximately 50 nm for typical DMOAP surface anchoring strength of 0.1 mJ/m\(^2\)), defect formation should no longer be energetically favourable.[24] However, there is some evidence to the contrary. For instance, Ryzhkova et al. [25] used video-tracking dark-field microscopy to demonstrate that silane-modified nanoparticle silica interactions could be measured and their pair-binding energies were reported for diameters as low as 35 nm. Surprisingly, they even observed the dipolar defect configuration and the formation of dipolar chains for particles smaller than 100 nm, in contradiction to the size dependence observed for larger particles in earlier work. Škarabot et al. [26] also reported dipolar chaining of DMOAP-modified silica nanoparticles of diameter 125 nm using polarising microscopy and observed a clear satellite defect consistent with the formation of a dipole. Nevertheless, such microscopic observations of defect formation around nanoparticles are restricted to very dilute systems. The defect structures formed at high nanoparticle loadings, necessary to achieve appreciable change in device performance, are unknown.

There is a long history of using both small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering to study liquid crystal phase behaviour of both thermotropic liquid crystals [27] and lyotropic suspensions of rod [28,29] and plate-like particles. [30,31] This is because the length scales associated with liquid crystal phases are readily accessible to X-ray scattering techniques (\( d \)-spacing between 5 and 5000 Å). In addition, high sample concentrations are easily studied, which makes the technique suitable for the study of lyotropic phase behaviour. Although SAXS techniques are ideally suited to study nanoparticle structures,[32,33] there is considerably less literature available on the study of particle – liquid crystal composites using X-ray scattering methods. Composites of liquid crystal and anisometric pigment particles have been studied under electric field using SAXS, which showed cooperative, tuneable alignment between the pigment particles and the nematic director.[34] Recent work has also demonstrated that liquid crystal-driven assembly of gold nanorods can be measured using SAXS.[35] Gold nanorods self-assembled into hexagonal clusters in a liquid crystal which could be aligned with an electric field. These clusters attained significantly higher order parameters in an applied field when in a liquid crystal than when in an isotropic solvent, in which they did not assemble into clusters.

In this work, we perform SAXS experiments on electric field-aligned 4-pentyl-4-cyanobiphenyl (5CB)–silica nanoparticle composites. This investigation represents an advance in our work on electric field-aligned liquid crystal–nanoparticle composites. We are not aware of any other report of X-ray scattering studies of aligned nematic liquid crystal–spherical nanoparticle composites and no other SAXS measurement of defect assemblies of spherical nanoparticles. The electric field-induced alignment of liquid crystal–silica nanoparticle aggregates has been studied using an electric field cell together with synchrotron X-ray scattering. SAXS patterns are fitted to a paracrystalline chain structural model and characterised in terms of their degree of alignment, aggregate orientation relative to the director, lattice spacing within the aggregate and average aggregate size and shape. This has allowed us to demonstrate for the first time that nematic director-driven assembly occurs for spherical silica nanoparticles in a bulk sample of nematic liquid crystal and to identify that the quadrupolar defect interaction is responsible for the formation of these structures in agreement with the expected behaviour for sub-100 nm diameter DMOAP-modified silica nanoparticles but in contradiction to previous experimental work.

2. Experimental

2.1 Materials

Colloidal amorphous silica nanoparticles of density 2 g/cm\(^3\) and approximate diameters 50 and 100 nm were obtained from Polysciences (Eppelheim, Germany). 5CB was obtain from Kingston Chemicals (Hull, UK) and was used as received. DMOAP was obtained from Sigma Aldrich (St Louis, MO, USA) as a 42% by weight solution in methanol. High pressure liquid chromatography (HPLC) grade methanol for solvent transfer was obtained from Sigma Aldrich.

2.2 Sample preparation

In order to generate strong homeotropic anchoring on the surface of the silica nanoparticles in a nematic liquid crystal, their surfaces were modified using DMOAP. A concentrated solution of
DMOAP in methanol was added to a dilute aqueous suspension of colloidal silica particles to produce a final DMOAP concentration of 1% by weight. The resulting suspension was stirred for 20 min at room temperature. The particles were then concentrated via sedimentation, and the supernatant was replaced with fresh distilled water six times. The particles were then dried under vacuum at 120°C and redispersed at known concentrations in HPLC grade methanol as a carrier solvent. To produce liquid crystal–nanoparticle composites, a known weight of particle suspension in methanol was added to a sample of liquid crystal and stored under vacuum at 35°C to evaporate the carrier solvent. Evaporation was continued until the mass of the sample indicated that >99% of the solvent had been removed. The samples were removed from the vacuum oven and thoroughly mixed through a combination of sonication, vortex mixing and stirring before use. This approach was used to ensure that the particles were well dispersed as a suspension in a carrier solvent before addition to the liquid crystal and was found to be a faster, more consistent method to create well-dispersed samples than the alternative approach of adding the particles as a dry powder. It also allowed for very accurate determination of the particle volume fraction $\eta$ compared to adding a small amount of dry powder to <1 ml of liquid crystal. For SAXS measurements, the samples were contained in 1.5 mm quartz-glass capillary tubes (Capillary Tube Supplies, Bodmin, UK) via pipette.

2.3 Sample characterisation

SAXS was used to determine the size and polydispersity of the nanoparticles. The analytical scattering factor for polydisperse spheres proposed by Sheu et al. [36,37] was fitted to the scattered intensity from dilute suspensions of silica nanoparticles in methanol. The particle mean diameters and the standard deviations of their size distributions were determined to be 105 ± 7 and 48 ± 11 nm, respectively. These values were used throughout the analysis. Scanning electron microscopy was also used to verify the size and shape of the silica nanoparticles (see Supplemental data).

2.4 Small-angle X-ray scattering

2.4.1 SAXS measurement

The SAXS measurements were performed at Diamond Light Source, Harwell Science and Innovation Campus (Didcot, UK) on the I22 beamline with a sample to detector distance of 10 m and beam energy of 8 keV. The scattered X-rays were detected using a Dectris Pilatus 2 M detector (Baden, Switzerland). Data were reduced using in-house IDL scripts. For a typical experiment, measurements were performed with 10-second exposures, and each scattering pattern was averaged over 10 measurements, which was found to cause no noticeable X-ray damage to the sample. A transmission-normalised solvent background was subtracted from the data, and sections of the image not caused by X-ray scattering, such as the beamstop, were masked out of the analysis.

2.4.2 Sample stage

In order to macroscopically align the liquid crystal, a bespoke sample stage was used which produced an aligning electric field. The geometry of the stage is shown schematically in Figure 1. It consisted of two Kapton-coated brass parallel plate electrodes (diameter approximately 8 mm) separated by 2 mm. Electric fields were produced using an Agilent 33210A function generator (1–8 Vpp with sinusoidal waveforms of frequency 1 kHz) (Santa Clara, CA, USA) amplified by a Trek Model 609E-6 high-voltage amplifier (1000× gain) (Lockport, NY, USA). The signal generator was monitored using a

![Figure 1. Schematic of the electric field stage used for the X-ray scattering measurements, in the coordinate system used for the analysis and simulations. The X-ray beam, sample and detector centre are aligned along the x-axis. Angle $\alpha$ defines the local director in the $xy$ plane and $\beta$ is the angle between the local director and the $z$-axis. The azimuthal angle of the scattering on the detector is denoted $\phi$.](image)
Tektronix TDS210 oscilloscope (Beaverton, OR, USA). This geometry was capable of generating electric fields of up to 4 MV/m across the sample.

3. Results and discussion

The scattering from a suspension of 105 nm diameter silica nanoparticles in nematic 5CB with an applied field is shown in Figure 2b–d. The scattering is anisotropic at low \( Q \) and extended in the \( Q_z \) direction, which indicates that the particles have formed structures which are extended in the \( y \)-axis, perpendicular to the applied field. In Figure 2b, the alignment is already considerable for an applied field of 0.25 MV/m. It becomes slightly better aligned at the higher field strengths of 1 and 4 MV/m in Figure 2c and 2d, respectively, as shown by the increased aspect ratio of the central peak. If the assembly or reorientation was due to chaining of electrically induced dipoles, then the assembly axis would be parallel rather than perpendicular to the field direction [38] when the field was applied and no assembly would be observed before the field was applied, giving an isotropic scattering pattern. However, with no field applied (Figure 2a), the scattering is not isotropic, but appears to be a superposition of a few patterns like Figure 2d but rotated by different angles. This is consistent with a sample containing several differently oriented regions of nematic, and within each of these regions the nanoparticles have assembled into structures that are extended perpendicular to the local director. When an electric field is applied, it aligns the directors of the nematic domains and in order to minimise the director distortion, these particle aggregates then rotate and reorient, forming a macroscopically aligned population of particle structures (Figure 3). The occurrence of rigid body-like rotation of defect-bound structures has been demonstrated previously in a thin liquid crystal cell for complex defect-bound structures [20] and for nanoclusters of gold nanorods in a bulk sample.[35] The evidence for particle assembly with no applied field is confirmation that the structure assembly mechanism originates from the liquid crystalline medium rather than the electric field. For the same concentration of particles in methanol, the scattering pattern is isotropic and identical with and without an applied field. The scattering patterns for \( \eta = 0.002, 105 \text{ nm DMOAP-modified silica in 5CB liquid crystal at (a) zero applied field, (b) 0.25 MV/m, (c) 1 MV/m and (d) 4 MV/m. The black stripe at } Q_y = 0.0065 \text{ Å}^{-1} \text{ is a gap in the sensitive area of the detector.}
electric field, which further confirms that the assembly mechanism is liquid crystal based (see Supplemental data). Furthermore, extended structure perpendicular to the nematic director is evidence that the particle structure orientation is coupled to the nematic director, as would be expected for a particle structure induced by the interaction of defects.

3.1 Self-assembled defect structures

A colloidal particle with homeotropic anchoring embedded in a nematic will generate either a dipole or a quadrupole defect. The defects on different particles can interact, resulting in complex, thermally stable structures. The assembly scattering observed in Figure 2 is consistent with a system of quadrupolar defects, which can produce particle structures that are highly extended perpendicular to the director. Dipolar defects, on the other hand, form different structures depending on whether the dipoles are parallel or antiparallel. A suspension of parallel dipolar defects (dipole satellite defects on the same side of the particle) would primarily form defect chains parallel to the director. While it is possible for dipolar defects to form structures perpendicular to the nematic director through the antiparallel dipole configuration, a system of particles occupying dipolar defects would assemble into a diverse range of structures – including structures parallel and perpendicular to the director, as well as highly branched structures.[39] Therefore, it is unlikely that this experimental system consists primarily of dipolar defects, because to reproduce the observed scattering pattern, it would be necessary for all dipole aggregate structures to grow in the antiparallel dipole configuration. However, dipolar defects may be accommodated in quadrupolar defect structures [40] while still maintaining a structure with its primary axis perpendicular to the nematic director, so a secondary population of dipolar defects could still be present.

This tendency for structures to align perpendicular to the electric field was consistent across different particle sizes, particle volume fractions and electric field strengths, which indicates that quadrupolar defects readily form and interact for DMOAP-modified nanoparticle silica in 5CB. To confirm that the observed scattering was consistent with a system of particle chains and to determine their degree of alignment, a structural model was produced and compared with the observed scattering data.

3.2 Structural analysis

Structural models of chains of spheres, either randomly oriented [41–43] or perfectly oriented along a field axis,[44] have been produced previously. In this section, we will describe a structural model which can be continuously varied between perfect alignment along the field axis, random orientation and alignment perpendicular to the field axis.

To analyse the scattering by a system of aligned spheres, we used a paracrystalline structure factor for a chain of polydisperse spheres with an orientational distribution for the chain axis. The structure was modelled as chains of spheres whose centres were separated by a vector \( \mathbf{a} \). Following Hosemann,[45] it was assumed that the longitudinal and transverse components of this vector were distributed according to a Gaussian distribution. The spheres were assumed to be polydisperse with a Schultz distribution. Furthermore, it was assumed that the inter-chain interference could be ignored because the suspension was dilute.

3.2.1 Structural model

The structure factor for a single chain of a given orientation and length \( L \) is as follows [46]:

\[
S_n(Q) = n + 2 \sum_{m=1}^{n-1} (n-m) \cos(Q_L a_m) \exp \left( -\frac{Q_L^2 \sigma_L^2 m}{2} \right) \exp \left( -\frac{Q_T^2 \sigma_T^2 m}{2} \right)
\]

where length \( L = (n-1)a \), \( n \) is the number of particles in the chain, \( a \) is the mean periodicity, \( m \) is the particle number within the chain, \( \sigma_L \) is the longitudinal distortion, \( \sigma_T \) is the transverse distortion, \( Q_L \) is the scattering vector component along the mean chain
axis and $Q_T$ is the transverse component. The structure factor for different lengths is given by:

$$ S(Q) = \sum_{n_{\text{min}}}^{n_{\text{max}}} f_n S_n(Q) $$  \hspace{1cm} (2)

where $n_{\text{min}}$ and $n_{\text{max}}$ are the number of particles in the shortest and longest chains, respectively, and $f_n$ is the fraction of chains containing $n$ particles. It was assumed that $f_n$ is uniform between $n_{\text{min}}$ and $n_{\text{max}}$.

The structure factor is calculated for all orientations and weighted by the orientational distribution function of the chain axis as:

$$ g(\beta) = Z^{-1} \exp(\cos^2 \beta) $$  \hspace{1cm} (3)

where $\beta$ is the angle between the chain and the overall director, $r$ is a coefficient that determines how ordered the system is and $Z$ is a normalisation constant.

The order parameter $\chi$ can then be calculated using Hermans' [47] orientation parameter as follows:

$$ \chi = (3\langle \cos^2 \beta \rangle - 1)/2 $$  \hspace{1cm} (4)

where $\langle \cos^2 \beta \rangle$ is given by:

$$ \langle \cos^2 \beta \rangle = \frac{\int_0^{\pi} g(\beta) \cos^2 \beta \sin \beta d\beta}{\int_0^{\pi} g(\beta) \sin \beta d\beta} $$  \hspace{1cm} (5)

The scattering intensity is finally calculated by multiplying the orientationally averaged structure factor by the analytical form factor for polydisperse spheres as:

$$ I(Q) = A \langle S(Q) \rangle_{\alpha, \beta} F^2(Q) $$  \hspace{1cm} (6)

where $\langle S(Q) \rangle_{\alpha, \beta}$ indicates the orientational average over angles $\alpha$ and $\beta$, $F^2(Q)$ is the scattering factor from polydisperse spheres and $A$ is a scaling factor.

In order to test this model, $I(Q)$ was calculated as a 2D intensity map and compared with data. The simulated scattering patterns are shown in Figure 4. Figure 4a shows the scattering for an unaligned system, which is isotropic with a maximum at $Q = 0 \text{Å}^{-1}$. The scattering pattern for a system of perfectly aligned chains parallel to the electric field is shown in Figure 4b, but this is not seen in our experimental data. The scattering for a system of highly aligned chains perpendicular to the field direction is shown in Figure 4c, and this does resemble our experimental data. It should be noted that the reduction in central peak sharpness in Figure 4c compared to Figure 4b is because the director is uniformly distributed perpendicular to the $z$-axis. In this case, the chains are highly aligned perpendicular to the field but can take any direction perpendicular to it with equal probability.

The intensity profile along the $Q_y$ axis at $Q_z = 0 \text{Å}^{-1}$ was also generated for a range of lengths and distortion parameters. Figure 5 shows the projected intensity as a function of $Q_y$ for a chain of length 400 nm and a chain of length 2000 nm both with periodicity $a = 100 \text{nm}$ and with different values for the longitudinal distortion parameter $\sigma_L$. The section shows a peak corresponding to the particle spacing at $Q_y$ of approximately $0.006 \text{Å}^{-1}$ (approximately $2\pi/a$) and oscillations that flatten out with increased distortion and length. Figure 6 shows the vertical scattering profile for chains of different length but with longitudinal distortion parameter.

Figure 4. 2D-simulated scattering patterns for the total scattering from particle chains with length distributed evenly between 200 and 1000 nm with periodicity 100 nm, longitudinal distortion 20 nm, transverse distortion 20 nm, particle diameter 100 nm (5% polydispersity) and chain axis order parameters of (a) 0, (b) 1 and (c) -0.5.
σ_L = 17 nm. Again, the scattering profile shows a strong peak corresponding to the particle lattice spacing at Q = 0.006 Å⁻¹, but the secondary oscillations for Q < 0.006 Å⁻¹ are differently spaced for the different length structures. The scattering intensity for different lengths is monotonically decreasing for 0.002 Å⁻¹ < Q < 0.005 Å⁻¹, and the structural peak at Q = 0.006 Å⁻¹ is more strongly suppressed for shorter chains. The central maximum of the scattering at Q = 0 Å⁻¹ tends towards the number of particles squared times the form factor of the sphere, so longer chains have a more intense central peak (Figure 6).

However, for the Q range accessible in a typical scattering experiment (Q > 0.001 Å⁻¹), this central peak is not captured; therefore, we see that the scattering profile is nearly identical in shape (but offset in intensity) for chain lengths in excess of 1000 nm for the experimentally accessible values of Q.

### 3.2.2 Test of structural model

One-dimensional scattering profiles along the Q_y- and Q_z-axes from the data set portrayed in Figure 2d are shown in Figure 7, along with the one-dimensional scattering curve for the silica nanoparticles in methanol. The Q_y section is monotonically decreasing at low Q_y followed by a flat region for Q_y = 0.005–0.007 Å⁻¹. This indicates that the aggregate length is broadly distributed rather than monodisperse, because there are no periodic fringes below Q_y = 0.007 Å⁻¹, and the initial decrease at low Q_y results from the combined contribution of multiple short chain lengths (Figure 6), where the slope is simply dependent on the distribution of sizes. The gradient of the horizontal section Q_z is weakly dependent on the transverse distortion for a highly ordered system and more strongly dependent on the average length of the aggregates.

Figure 8 shows that the structural model is in good agreement for the experimental data presented in Figure 2b. The order parameter of the chains was −0.49. The chain lengths were distributed between 321 and 535 nm with periodicity 107 nm and a longitudinal distortion of 13 nm. Longer chains introduced a steeper gradient for Q < 0.005 Å⁻¹ than was present in the data. This suggests that the...
particles are assembling into particle chains of four to six particles, in good agreement with dark-field microscopy and polarising microscopy images published elsewhere.\[25\] Full-fit parameters are given in Table 1, fit a.

Small deviations between the structural model presented here and the experimental data can be attributed to several factors. First, the structural model presented here does not include the effect of inter-chain interactions, which are known to be present in a nematic liquid crystal.\[18\] Second, the distribution of chain lengths may be more complex than that used here. A Gaussian distribution was also tested but was not found to improve the fit quality significantly. The influences of wall-anchoring of the director and particles adsorbed onto the capillary surface are also not considered. Finally, the distribution of particle sizes is uncorrelated with the lattice distortion in this model, which could be more significant for a highly polydisperse system.\[41\]

### 3.3 Order parameter of aggregate structures

Using the structural model, we can determine the degree of order present for different voltages and particle concentrations. For the dilute 105 nm particle system, we see very little voltage dependence for the degree of induced anisotropy above a threshold value (Figure 9a). For larger particle concentrations, however, we see less overall anisotropy and some voltage dependence (Figure 9b-d). This reduction in order parameter is shown as a function of voltage for different particle systems in Figure 10 and could be due to several factors. The smaller 48 nm diameter particles clearly show both a reduction in order parameter and some voltage dependence in Figure 9c and 9d compared to the dilute 105 nm particles in Figure 9a. This suggests that, rather than a ‘Fréedericksz-like’ transition of non-interacting particle chains shown by the 105 nm particles, these systems have an additional elastic component that is preventing the particle chains from reorienting. If we consider the fitted-order parameter, we see that although the values reflect the observed behaviour in the angular regroups, the fit does not reproduce the two-dimensional profile at low \(Q\). By including an additional fraction \(F_0\) of particle chains with an order parameter of 0 in our structural model, we find that the structural peak at low \(Q\) is more accurately reproduced (Figure 11), and the order parameter of the chains that are free to align with the

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### Table 1. Sample parameters used to fit a: 105 nm diameter nanoparticles, \(\eta = 0.002\); b: 48 nm diameter nanoparticles, \(\eta = 0.003\), both at 4 MV/m and b*: the same sample system as b, but fitted with an additional unaligned chain population fraction \(F_0\).

| Fit | Diameter ± standard deviation (nm) | \(a\) (nm) | \(\sigma_L\) (nm) | \(\sigma_T\) (nm) | \(r\) | \(\delta\) (deg) | \(L_{\text{min}}\) (nm) | \(L_{\text{max}}\) (nm) | \(F_0\) |
|-----|------------------------------------|-----------|-----------------|-----------------|------|----------------|----------------|----------------|-------|
| a   | 105 ± 7                            | 107       | 13.0            | 25.0            | −85.6| −5.6           | 321            | 535            | 0     |
| b   | 48 ± 11                            | 55        | 8.6             | 10.2            | −2.9 | 0              | 110            | 770            | 0     |
| b*  | 48 ± 11                            | 55        | 8.8             | 10.5            | −14.5| 0              | 110            | 550            | 0.3   |

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Figure 8. (a) SAXS scattering pattern for \(\eta = 0.002\) and 105 nm DMOAP-modified silica in 5CB liquid crystal at 4 MV/m, (b) \(Q_y\), (c) \(Q_z\) data and fit and (d) simulated scattering pattern for fitted parameters given in Table 1, fit a.
liquid crystal is much greater, with electric field dependence similar to that of a dilute system (Figure 10). This observation is compatible with a system of ‘defect-bound soft solids’ demonstrated by Wood et al.[48] where particle chains have reached sufficient length and density to bind together, forming a tangled, gel-like network. This network has a global order parameter of 0, but both particle chains in locally dilute sections (voids in the gel network) of the sample and more diffuse sections of the gel (chains only weakly or partially connected to the network) are able to rotate or deform, respectively, under an applied electric field. As the particle concentration increases, dilute regions and more diffuse sections of the gel become less common, and so the system is less able to respond to an applied field. This response to electric field with increased particle concentration is demonstrated for both 105 and 48 nm particles. The onset of a gel-like regime at lower volume fractions in the smaller particle case may be attributed to the ‘effective size’ of a particle defect; the volume of a particle defect is dependent on the elastic properties of the liquid crystal rather than particle size for small particles, so for a fixed volume fraction of particles the effective volume fraction of defects would be an order of magnitude greater for 48 than for 105 nm particles, due to the higher number density of the smaller particles.

4. Conclusion

In this work, we have shown that SAXS can be used to study nanoparticle defect structures in a nematic liquid crystal. The scattering from a suspension of silica nanoparticles in nematic 5CB is reproduced

Figure 9. (colour online) Azimuthal intensity distribution for $Q = 0.003\,\text{Å}^{-1}$, for 105 nm silica in 5CB at volume fractions (a) 0.002 and (b) 0.005 and for 48 nm silica in 5CB at volume fractions (c) 0.003 and (d) 0.006.

Figure 10. Chain axis order parameter as a function of electric field for $\eta = 0.002$, 105 nm particles and $\eta = 0.003$, 48 nm particles. The order parameter of the 48 nm particles was determined using both the same structural model as the 105 nm particles and a second structural model which included a population of unaligned particle chains.
using a model of polydisperse spheres located at the lattice points of a highly aligned, paracrystalline linear chain. The nanoparticles assemble into particle chains in a macroscopically unaligned nematic, where the chains display an overall order parameter of approximately 0. Upon application of an electric field, the local director (responsible for initial chain formation) aligns with the field, and the nanoparticle assemblies align with an order parameter in between \(-0.45\) and \(-0.5\), with their primary axes perpendicular to the director. This suggests that the nanoparticles are forming defects in the liquid crystal predominantly in the quadrupolar configuration rather than the dipolar configuration, which would be expected to assemble into chains parallel to the director. The observation of perpendicular alignment is contrary to recent work\[25,26\], which suggests that dipolar defect configurations are common in silica nanoparticle suspensions in nematic liquid crystals. The reasons for this disparity in behaviour are not clear, but the difference may be due to confinement biasing the defect type in a thin cell, which is known to alter the defect configuration for larger microparticles\[15\] or the high shear experienced by the defects as the cell is loaded. We expect these effects to be less important in the bulk sample reported here. We observe that higher particle loadings decrease the alignment of the paracrystalline chains but develop some electric field dependence. This reduction in overall alignment but more pronounced electric field dependence could be attributed to the formation of an increasingly jammed network as chains percolate throughout the liquid crystal and begin to interconnect, both reducing the number of chains that are free to align and forming an unaligned structure. In these cases, the scattering could be approximated by a mixture of highly ordered free chains and a population of unaligned chains. The structural model was modified to include an additional population of unaligned chains which was found to better reproduce the experimental data at higher nanoparticle loadings. At low particle concentrations, the proportion of unaligned chains dropped to zero. These findings demonstrate that a rich variety of liquid crystal–nanoparticle composite self-assembled structures can be studied quantitatively using SANS. Our approach is ideally suited for the study of nanoscale structure inaccessible or difficult to study by conventional microscopy methods and could be particularly useful for studying the long-term stability of nanoparticle-doped liquid crystals.

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Supplemental data

Supplemental data for this article can be accessed here.

References

[1] Hegmann T, Qi H, Marx VM. Nanoparticles in liquid crystals: synthesis, self-assembly, defect formation and potential applications. J Inorg Organomet Polym Mater. 2007;17:483–508. doi:10.1007/s10904-007-9140-5
[33] Park SY, Lytton-Jean AKR, Lee B, Weigand S, Schatz GC, Mirkin CA. DNA-programmable nanoparticle crystallization. Nature. 2008;451:553–556. doi:10.1038/nature06508

[34] Greasty R, Richardson R, Klein S, Cherns D, Thomas M, Pizyzy C, Terrill N, Rochas C. Electro-induced orientational ordering of anisotropic pigment nanoparticles. Philos Trans R Soc A. 2013;371:20120257. doi:10.1098/rsta.2012.0257

[35] Thomas MR, Klein S, Greasty RJ, Mann S, Perriman AW, Richardson RM. Nematic director-induced switching of assemblies of hexagonally packed gold nanorods. Adv Mater. 2012;24:4424–4429. doi:10.1002/adma.201201319

[36] Kotlarchyk M, Chen S-H. Analysis of small angle neutron scattering spectra from polydisperse interacting colloids. J Chem Phys. 1983;79:2461. doi:10.1063/1.446055

[37] Sheu EY. Polydispersity analysis of scattering data from self-assembled systems. Phys Rev A. 1992;45:2428–2438. doi:10.1103/PhysRevA.45.2428

[38] Vutukuri HR, Demiroers AF, Peng B, Van Oostrum PDJ, Ilmohf A, Van Blaaderen A. Colloidal analogues of charged and uncharged polymer chains with tunable stiffness. Angew Chemie. 2012;124:11411–11415. doi:10.1002/ange.201202592

[39] Pishnyak O, Shiyazovskii S, Lavrentovich O. Inelastic collisions and anisotropic aggregation of particles in a nematic collider driven by backflow. Phys Rev Lett. 2011;106:047801. doi:10.1103/PhysRevLett.106.047801

[40] Ognysta U, Nych A, Nazarenko V, Škarabot M, Muševič I. Design of 2D binary colloidal crystals in a nematic liquid crystal. Langmuir. 2009;25:12092–12100. doi:10.1021/la901719t

[41] Chiappisi L, Prévost S, Gradzielski M. Form factor of cylindrical superstructures composed of globular particles. J Appl Crystallogr. 2014;47:827–834. doi:10.1107/S1600576714005524

[42] Chiappisi L, Prévost S, Grillo I, Gradzielski M. Chitosan/alkylethoxy carboxylates: a surprising variety of structures. Langmuir. 2014;30:1778–1787. doi:10.1021/la404718e

[43] Kawaguchi T. Scattering curve and radius of gyration of a straight chain of identical spheres. J Appl Crystallogr. International Union of Crystallography. 2001;34:771–772. doi:10.1107/S0021889801014558

[44] Jain N, Liu CK, Hawkett BS, Warr GG, Hamilton WA. Application of small-angle neutron scattering to the study of forces between magnetically chained monodisperse ferrofluid emulsion droplets. J Appl Crystallogr. 2014;47:41–52. doi:10.1107/S1600576713030045

[45] Hosemann R, Bagchi SN. Direct analysis of diffraction by matter. Amsterdam: North-Holland Publishing; 1962.

[46] Guinier A. X-ray diffraction in crystals, imperfect crystals, and amorphous bodies. San Francisco (CA): W.H. Freeman and Co.; 1963. Chapter 9, Crystal imperfections destroying long range order; p. 295–305.

[47] Hermans PH. Physics and chemistry of cellulose fibres. New York (NY): Elsevier; 1949.

[48] Wood TA, Lintuvuori JS, Schofield AB, Marenduzzo D, Poon WCK. A self-quenched defect glass in a colloid-nematic liquid crystal composite. Science. 2011;334:79–83. doi:10.1126/science.1209997