Highly Confined Stacks of Graphene Oxide Sheets in Water

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Abstract Since the discovery of graphene oxide (GO), the most accessible of the precursors of graphene, this material has been widely studied for applications in science and technology. In this work, we describe a procedure to obtain GO dispersions in water at high concentrations, these highly dehydrated dispersions being in addition fully redispersible by dilution. With the availability of such concentrated samples, it was possible to investigate the structure of hydrated GO sheets in a previously unexplored range of concentrations, and to evidence a structural phase transition. Tentatively applying models designed for describing the small-angle scattering curve in the Smectic A (or Lₕ) phase of lyotropic systems, it was possible to extract elastic parameters characterising the system on the dilute side of the transition, thereby evidencing the relevance of both electrostatic and steric (Helfrich) interactions in stabilising aqueous lamellar stacks of GO sheets.

1 Introduction

Graphene oxide (GO) is a material obtained by mild oxidation and exfoliation of graphite, and one of the most common manners of preparing it is Hummer’s modified method [1, 2]. This material is attracting a lot of interest, in particular because it can easily be dispersed in various solvents, including water, and many GO-based materials and composites have been developed by solution processing [3–8].

The structure of GO sheets, as well as their structural organisation in water have been investigated using various techniques, including atomic force microscopy (AFM), polarised optical microscopy (POM), circular dichroism (CD) and small-angle x-ray scattering (SAXS)–see for instance [4, 6, 9–14]. Most of these works–either directly (AFM) or indirectly (SAXS)–point to an atomic thickness t for the GO sheet, significantly below 1 nm (assuming for the GO density ρGO a value around 1.8 g/cm³ in the SAXS-based method). Furthermore, it is now a consensus from POM and SAXS studies that the phase diagram of the lyotropic GO–water dispersion exhibits isotropic, nematic and lamellar (or lamellar-like) phases, phase transitions being driven by the increase of GO concentration in the dispersion, as also observed in somewhat similar materials made of planar, solid-like sheets of near-atomic thickness [15–17]–or a bit thicker [18].

In qualitative accordance with Onsager’s theory for the isotropic-to-nematic phase transition in suspensions of hard colloids, quantitatively valid for slender particles [13], the particle volume fraction ϕ₁ at the transition onset is given in numerical simulations for “pancake” particles by [19–21]

\[ ϕ₁ ≈ \frac{3.2}{L} \]  

in terms of the particle aspect ratio L/t. Equation (1) describes reasonably well the mass fraction f_B of GO when birefringence first occurs (viz., when the nematic phase first appears) using \[ f_B = ϕ₁ \times ρGO/mGO \], considering the dispersity ϕ in lateral extensions L [22, 23], as well as uncertainties in GO thickness t and density ρGO. Such an agreement is considered as a convincing argument for the GO sheets being rigid enough to remain essentially uncrumpled in dilute suspensions [4–6].

Structures commonly described as lamellar are observed in more concentrated GO dispersions, as mainly results from SAXS studies [6, 8, 12, 21]. A behaviour also found in similar (inorganic) materials such as phosphatoantimonates, clays or titanium-iron acid oxides [15–17, 24]. The structure (sometimes depicted more cautiously as a nematic gel, a locally layered system, or a pseudo-smectic phase because compelling evidence for positional long-range order is not easily found) is formed by stacking GO sheets (or other kinds of solid-like sheets), separated by layers of water, with a given distance of repetition t of the unit cell along the stacking axis z. In the plane perpendicular to z, the structure of the two-dimensional solid-like sheet is well-defined locally, but more difficult to ascertain at scales larger than L. Owing to the repulsive interaction along z between two facing sheets, with a significant electrostatic contribution according to refs. [6, 15, 16], the
thickness of the water layers increases, with therefore an increase in \( \ell \), when (low ionic strength) water is added to the system. In a geometric description of the swelling process where \( L \rightarrow \infty \) and \( t \) is a constant, a simple dilution law, namely
\[
\ell = t/\varphi
\] (2)
is expected and indeed observed, as in refs. [6][12], at least for a restricted range of particle volume fractions \( \varphi \), see [13][16]. The dilution law, eq. (2), yields the above-mentioned SAXS (indirect) estimate for the GO sheet thickness \( t \).

One of the purpose of the present contribution is to explore the validity of eq. (2) towards more concentrated GO dispersions than previously investigated. In the next sections, we describe how our samples are characterised using dynamic light (sect. 2.1) or small-angle x-ray (sect. 2.3) scattering techniques, and dehydrated in a controlled way to almost complete dryness while remaining fully dispersible in water (sect. 2.2). Our main results are summarised in sect. 3.1, with evidences for a structural phase transition between lamellar structures, not reported previously, as dehydration proceeds. In sect. 3.2 we discuss possible mechanisms stabilising in water the lamellar stacks of GO sheets, drawing an analogy with lamellar stacks of self-assembled amphiphilic bilayers. Though we give no clues as regards the most concentrated regime, the lamellar stack of GO sheets appears to be well described in the dilute regime by the so-called “unbinding transition” phenomenon that results from repulsive HELFICH [26] and electrostatic interactions between stacked layers competing with attractive VAN DER WAALS interactions [27][28].

2 Materials and methods

2.1 Sample characterisation

The graphene oxide suspensions are prepared from a commercial aqueous solution sold by Graphenea (San Sebastian, Spain), with nominal concentration 4 mg/mL. Such a solution is concentrated enough to be birefringent, as revealed by POM, but does not yet exhibit any significant increase in viscosity compared to water. According to the producer, the dispersion presents more than 95% of carbon monolayers and an amount between 41 and 50% of oxygen atoms, with variable sheet dimensions \( L \) below 10 \( \mu m \), usually around 1–2 \( \mu m \) [29]. Owing to the presence of COOH groups attached to the sheet surface, the aqueous GO suspensions are expected to be acid and, indeed, their measured \( \text{pH} \) is about 2.4. Two different batches were bought and used to prepare the samples. For both batches, dynamic light scattering (DLS) experiments were carried out, using a research goniometer and laser light scattering system from Brookhaven Instruments Corporation (Holtsville, NY, USA). Freshly prepared samples were diluted in water to 0.04 mg/mL. At such a concentration, the samples are no longer birefringent but faint depolarised fluctuations can be observed by POM in an optically thick (800 mm) cell from VitroCom (Mountain Lakes, NJ, USA). The DLS experiment is performed with incident light polarised perpendicular to the scattering plane, without analysing the polarisation of the scattered signal. DLS experiments have been repeated from time to time on ageing samples prepared with the first batch along a total period of about 2 months in an attempt to characterise ageing, if any. Some representative results on freshly prepared samples are shown in fig. 1. Fitting the DLS data to a stretched exponential model, see eq. 3, as a convenient (but ad hoc) way to somehow take into account the GO dispersity, two parameters (a characteristic time and a stretching exponent) were obtained as a function of the scattering wave vector \( q \).

The model correlation function is expressed as
\[
C(\tau) = \exp \left[ -2 \left( \frac{\tau}{\Delta} \right)^{\beta} \right]
\] (3)
where \( \Delta \) is the characteristic relaxation time and \( \beta \) the stretching exponent. Parameter \( \beta \) was found to decrease from ca. 0.9 to 0.7 as the scattering vector \( q \) increases from \( 1 \times 10^{-2} \) to \( 2.2 \times 10^{-2} \) nm\(^{-1}\). Besides, as illustrated in fig. 1 by the straight lines with a slope 2, the relaxation frequency \( \Delta^{-1} \) is proportional to \( q^2 \), meaning that an effective diffusion coefficient—or a hydrodynamic radius \( R_H \)—can be defined. From the standard Stokes-Einstein relation
\[
R_H = \frac{k_B T\Delta}{6\pi \eta} \times q^2
\] (4)
with \( k_B \) the Boltzmann constant, \( T \) the absolute temperature of the GO dispersion and \( \eta \) the solvent viscosity, hydrodynamic radii were found equal to 0.74 \( \mu m \) and 1.22 \( \mu m \) for batches 1 and 2, respectively.

![Figure 1](image-url)
As mentioned above, possible effects of ageing were checked on samples prepared from the first batch, with three distinct histories:

1. Samples were diluted to the concentration appropriate for DLS (ca. 0.04 mg/mL) immediately after receiving the solution from Graphenea, then stored for ageing;
2. Samples were diluted to the concentration appropriate for DLS from the solution stored for ageing received from the manufacturer;
3. Samples concentrated to ≈ 160 mg/mL immediately after reception of the Graphenea solution (see below, sect. 2.2, for details regarding the concentration procedure) were stored for ageing, then diluted to the concentration appropriate for DLS.

Whatever the sample history, the storage conditions were the same, namely stable temperature (22° C) and no exposure to direct light. In all cases, DLS did not reveal any significant ageing over a period of about 2 months.

### 2.2 Sample preparation

A procedure to increase the concentration of the commercial GO dispersions was implemented, requiring two steps. Centrifugation and ultracentrifugation are used in the first step. The commercial dispersion is first centrifuged for about 20 min at 1400g, in order to remove “large” aggregates from the sample. After discarding the bottom phase, the supernatant is then ultracentrifuged at a much higher speed (302000 g) for 5 h. The recovered supernatant, mostly water at pH = 2.6, occupying almost the total volume of the centrifuge cell, is also discarded. The remaining phase appears as a highly viscous material with a dark, almost black colour. As explained below—see also fig. 2—it turns out that the GO mass fraction $f_m$ achieved at this stage is around 0.16, thus corresponding to an increase in GO concentration by a factor about 40. We have checked on a few sacrificial samples, submitted to a somehow stronger vacuum (pressure in the mbar range) for about 15 h, that remaining water cannot be extracted with our set-up: Achieving complete dehydration would require ultra-vacuum or elevated temperatures. On the basis of our x-ray measurements (see below, Section 3.1), we estimate the weight fraction of “bound” water from Ref. [30] to be $f_w^\infty \approx 27.7\%$, with therefore $m(\tau) = (1 - f_w^\infty) \times m_\infty / m(\tau)$.

![Figure 2. GO mass fractions $f_m(\tau)$ as a function of the dehydration time in the vacuum chamber ($p = 300$ mbar) for three samples differing by their initial water content: ■ 14.4 %, □ 15.7 %, ▲ 17.6 %. The horizontal dashed line at $f_m = 0.723$ corresponds to the limiting GO mass fraction, and accounts for water molecules that cannot be removed with our drying set-up.](image)

Notably—and similarly to the first step—the second step of the dehydration procedure is reversible. As shown by SAXS (see below, sect. 3), adding water to a sample extracted at time $\tau_>$ from the desiccator in the required amounts to mimic the composition of a sample stored for a lesser time $\tau_<$ leads to essentially identical diffractograms for the “wet” and “dried-rehydrated” samples when they both originate from the same centrifuged material. At contrast with what has been observed with, e.g., freeze-dried GO dispersions where the GO chemical structure is strongly affected, it seems to be preserved in our case as no aggregates were found in the slowly dried samples redispersed in water.
2.3 Experimental techniques

Samples removed at time \( \tau \) from the desiccator were left for at least a week in their (now closed) preparation Eppendorfs to ensure relaxation of possible humidity gradients. After homogenisation, the samples were analysed by POM. Due to their extreme opacity when \( f_m \) exceeds 50\%, highly dehydrated samples could not be successfully observed. For samples with smaller mass fractions, images were recorded (data not shown) using an Olympus BX 51 microscope with crossed polarisers and a \( \times 20 \) objective. The samples were sandwiched between a glass slide and a coverslip, without special precautions for ensuring a constant optical path, estimated below 10 \( \mu \)m, but preventing water evaporation by means of a UV-curing glue. Birefringence was always observed, indicating a liquid-crystalline organisation. The samples were homogeneous, as revealed by observing them without the analyser, indicating that aggregates were not present. The samples were also investigated by small angle x-ray scattering. The thick pastes were spread on a circular (diameter 1.3 mm), machine-drilled opening perpendicular to the long axis of cylindrical stainless steel supports (2.0 × 20.0 mm) which were then introduced in quartz capillaries with a nominal diameter of 2.5 mm. The spreading procedure did not allow a control of the optical path better than \( \approx 25 \% \). The quartz capillaries were further flame-sealed, to ensure tightness. Diffractograms were recorded on a Bruker-AXS Nanostar machine equipped with a Hi-Star detector, also from Bruker (Karlsruhe, Germany). From the entrance pinhole to the beryllium window in front of the detector, the whole flight path is evacuated. A crossed-coupled pair of Göbel mirrors (Bruker) selects the \( \lambda = 1.5418 \) Å radiation of a copper source (Siemens), operated at 40 kV and 35 mA. A 3-pinhole system is used for collimating the incident beam, with a size (FWHM) at sample position ca. 0.43 mm in both vertical and horizontal directions. Two sample-to-detector distances, found close to 0.25 m and 1.05 m respectively, calibrated using silver behenate as standard \([34]\), were used to match the variable stacking periods of the samples. From the Gaussian width of the first order Bragg peak of silver behenate, we estimate a resolution width (FWHM) \( \Delta q \approx 5 \times 10^{-2} \) Å\(^{-1}\) or \( \Delta q \approx 6.0 \times 10^{-3} \) Å\(^{-1}\) for the two configurations, respectively. Owing to the intrinsic broadening of silver behenate \([34]\), the latter value could be slightly over-estimated. The scattering wave vectors that are practically accessible after subtracting the signal of a reference (water) capillary range from 0.04 Å\(^{-1}\) to 0.8 Å\(^{-1}\) in the “large-angle” configuration, and from 0.01 Å\(^{-1}\) to 0.2 Å\(^{-1}\) in the “small-angle” one. For accessing to even higher scattering wave vector values (typically 0.5–3.3 Å\(^{-1}\)), as required to assess the in-plane order of the GO sheets, we use a custom-made instrument with a copper rotating-anode-based setup and crossed-coupled pair of Göbel mirrors, both from Rigaku (Tokyo, Japan), a 3-pinhole collimation system similar to the Bruker one and a mar345 image plate detector (marXperts, Norderstedt, Germany) with sample-to-detector distance 0.15 m. At contrast with the Bruker system, only the collimation flight path is evacuated. Acquisition times on the instruments were in the order of 5 hours (Bruker Nanostar) or 1 hour (custom instrument). Temperature, fixed at 20°C, is controlled to within \( \pm 0.2 \)°C by a water circulation system (Bruker Nanostar) or, with a lesser precision, by the air-conditioning system of the room (custom instrument). For both instruments, the 2D detector images were most often characteristic of slightly oriented samples, as previously observed \([6,12]\), presumably because of the shear applied when filling the x-ray capillaries, or spreading the thick samples on the circular opening of the sample holders. Data was therefore azimuthally averaged to yield (normalised) intensities \( I \) vs. scattering wave vector \( q \) curves.

3 Experimental results and discussion

3.1 Results

SAXS results (“small” and “large” angle configurations) for ten selected samples are shown for illustration in fig. 3 in the \( I q^2 \) Kratyk representation that factorises out the characteristic \( 1/q^2 \) intensity decrease of very extended, thin and flat particles with random orientations \([35]\). The observed peak, characteristic of the lamellar stacking, moves towards higher scattering wave vector as dehydration proceeds. The second order peak, though clearly observed in either the “small” or “large” angle configurations for the two more hydrated samples in the corresponding series (GO mass fractions \( f_m \) 0.04 and 0.07, or 0.12 and 0.16, respectively), barely appears in the “large” angle configuration for the other samples—even though it still falls within the observation window. Nevertheless, as shown in fig. 4 with an observation window extending to much larger scattering wave vector values, the second order Bragg peak

![Figure 3. SAXS spectra (Kratky plot: \( I q^2 \) vs. \( q \)) for GO aqueous dispersions differing by their GO mass fractions \( f_m \): 0.04 (□), 0.07 (■), 0.10 (○), 0.14 (●), 0.12 (△), 0.16 (▲), 0.21 (◇), 0.26 (♦), 0.38 (◇) and 0.62 (▼). Data shifted vertically by amounts allowing a better visualisation.](image-url)
of the lamellar stacking, though weak, is clearly observed in one of the most dehydrated sample ($f_m = 0.792$). As features of the SAXS diffractograms may point to a structural phase transition. It is, however, not evidenced in the POM observations. We return to this intriguing point immediately below.

From Bragg’s law, namely $\ell = 2\pi/q_0$, it is found that, as expected, the period of the lamellar stack decreases when water is removed from the structure. The experimental dilution law $\ell(\varphi)$, with volume fractions $\varphi$ derived from mass fractions $f_m$ through the relation

$$\varphi = \frac{\rho_{H_2O} f_m}{\rho_{H_2O} f_m + \rho_{GO} (1 - f_m)}$$

(assuming volume additivity) is shown in fig. 6. A striking

a matter of fact, upon increasing the GO content up to $f_m \approx 0.23$, the intensity ratio between the second and first order peaks decreases until the second order peak apparently disappears, to be unambiguously recovered when $f_m$ reaches ca. 0.29. In this concentration range, the first order peak is also significantly broadened—see fig. 5. Such discontinuous behaviour near $\varphi \approx 0.14$ ($f_m$ close to 0.23) is clearly observed in the dehydrated limit of the dilution line. Besides, the discontinuity is precisely found to occur in the hydration range where broadening of the first order peak, as well as the disappearance of the second order peak have been observed, hinting again at the occurrence of a structural phase transition. Still, as evidenced in the inset to fig. 6 where SAXS data from samples submitted to the first concentration step (sect. 2.2)–some of them re-diluted–or only mildly dehydrated in the second step has been included, our data remains broadly compatible with the simple swelling law, eq. (2). This latter observation is nicely in agreement with the findings of previous studies, limited then to significantly more dilute GO dispersions [6,12] than investigated here. The fit to the dilution data leads to a sheet thickness $\ell \approx 2\pi/q_0$, or $0.17 \leq f_m \leq 0.29$. Data shifted vertically by amounts allowing a better visualisation

Figure 4. X-ray scattering data for the dryiest GO dispersion ($f_m = 0.792$). Lamellar stacking peaks marked by vertical arrows at $q_0 = 8.548 \times 10^{-1}\text{Å}^{-1}$ and $\approx 1.71\text{Å}^{-1}$. The 2D, in-plane order of the carbon atoms in GO sheets gives rise to the intense and thin peak observed at $q_0 = 2.964\text{Å}^{-1}$. Other intensity humps at $\approx 2.6\text{Å}^{-1}$: Unidentified features, possibly related to experimental artefacts arising from background scattering.

Figure 5. SAXS spectra in the Kratky representation for hydration values of the GO aqueous dispersions corresponding to a very broad first order Bragg peak. GO mass fraction $f_m$: 0.17 (○), 0.19 (▼), 0.21 (△), 0.23 (■), 0.26 (◇), and 0.29 (●). Data shifted vertically by amounts allowing a better visualisation

Figure 6. Stacking period $\ell$ as a function of the inverse volume fraction $1/\varphi$ for highly dehydrated GO dispersions ($0.1 \leq \varphi$, or $0.17 \leq f_m$). Inset: idem for the whole dilution range. Dashed line: Simple swelling law $\ell = t/\varphi$, drawn with $t = 0.39\text{nm}$.
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hexagonal structure of the carbon atoms in the graphene layers is observed using x-ray scattering at large angles. The peak found for \( q_c \approx 2.964 \, \text{Å}^{-1} \) can be related to the C–C nearest-neighbour distance \( d_{\text{C–C}} \) in a given graphene layer using \( 3d_{\text{C–C}} = 4\pi / q_c \), which indeed yields a result (1.41 Å) close to the commonly accepted value \( d_{\text{C–C}} = 1.42 \, \text{Å} \) [36]. The same result is found for more hydrated samples, as long as there is enough signal for this peak to emerge from the background.

Two peaks (locations \( q_0 = 0.85 \) and 1.71 Å\(^{-1} \), close to 2\( q_0 \)) can be found in the lower \( q \)-range part of fig. 6. They are related to the lamellar stacking order of the GO sheets. The corresponding periodicity, about 0.74 nm, is ca. 1.9× higher than the geometric parameter \( t \approx 0.39 \) nm found in fitting the simple dilution law to the whole set of SAXS data, that is to say about twice higher than the interlayer distance in graphite [36]. This result is to be attributed to the water molecules remaining trapped between the GO sheets, about 46% in volume fraction from eq. (2), a value found in rather reasonable agreement with eq. (5), leading to \( \varphi_w \equiv 1 - \varphi = 0.32 \).

3.2 Discussion

Despite a possible structural transition, occurring near \( \varphi = 0.14 \) and remaining to be characterised in details, it appears that GO aqueous dispersions exhibit a lamellar order over a quite extended concentration range, with a stacking period \( \ell \) varying from about 0.8 nm in the driest available system to more than 45 nm in our most hydrated samples. It is worth noting here that periods as large as \( \ell \approx 100 \) nm have even been found in other studies [6]. The physical mechanism stabilising the lamellar structure for vastly different water contents is therefore of obvious interest.

In the so-called lyotropic lamellar phases (self-assembled bilayers of surfactant or lipid molecules separated by layers of solvent, or solvent-swollen block-copolymer systems), a similar swelling of the lamellar structure over very extended composition ranges is also commonly observed [37–42]. It is similarly present in systems structurally similar to GO, viz. based on extended solid-like sheets–phosphoantimonate, for instance [15], or clay-based systems [16]—dispersed in aqueous solutions. Such a swelling is commonly attributed to long-range, either direct or effective, repulsive interactions between the stacked sheets, acting across the solvent layers and of electrostatic origin, or resulting from the “undulation interaction” mechanism proposed by Helfrich [26].

In the case of GO aqueous dispersions, the two mechanisms have already been identified [6, 15], at least indirectly in the case of Helfrich’s mechanism [43]. An electrostatic contribution is clearly evidenced when experimentally studying the swelling properties in the presence of added salts (in order to vary the ionic strength of the aqueous solvent layers). Using NaCl as a typical univalent salt in the (nominal) concentration range \( 10^{-6} \)–\( 10^{-1} \) M, the same effect as described in ref. [6] is observed here, namely a decreasing stacking period \( \ell \) with increasing salt content above a \( f_m \)-dependent salt concentration \( c^*_m \). In-

![Figure 7. SAXS spectra in the Kratky representation for GO aqueous dispersions differing in added NaCl content \( c_m \). GO mass fraction fixed to \( f_m = 4.3% \). Nominal salt concentrations \( c_m = 1 \times 10^{-6} \text{ M (●), 1 \times 10^{-5} M (□), 5 \times 10^{-5} M (▲), 1 \times 10^{-4} M (•), 5 \times 10^{-4} M (●), 1 \times 10^{-3} M (○), 5 \times 10^{-3} M (■), 5 \times 10^{-2} M (△) and 1 \times 10^{-1} M (▽). Data shifted vertically by amounts allowing a better visualisation. The vertical dashed line is drawn at \( q_0 = 3.49 \times 10^{-2} \, \text{Å}^{-1} \).](image)
the bending modulus $\kappa$ ("unbinding" tendencies) and the virial coefficient $\chi$ that encapsulates in the model the effect of interactions [25-46], in a way somehow similar to the theoretical approach to the lamellar–lamellar phase coexistence proposed in ref. [47].

As regards the salt effect on GO stacks, interpretations may be simpler than in refs. [44-46], at least if it is safe to assume that the main effect of salt (screening electrostatic repulsive interactions through the decrease of the Debye screening length) falls upon the parameter $\chi$ only, $\kappa$ being therefore unaffected. In such a simple limit, the MILNER–ROUX virial coefficient $\chi$ should be a monotonously increasing function of $c_s$, since VANDER WAALS attractions between GO sheets would be less and less counterbalanced by electrostatic repulsions [25], as classically described for colloidal particles in the DLVO theory [48]. The thermodynamic analysis of the unbinding transition then leads to a (schematic) phase diagram, displayed in the $(\phi, \chi)$-plane in fig. 8 following refs. [25,49].

The general features of the phase diagram are in qualitative agreement with available observations. As long as the salt concentration $c_s$ is low enough, interactions between GO sheets are essentially repulsive, $\chi$ should remain "small" (possibly negative) and the system is homogeneous–blank region in fig. 8. In this case, for any given $\ell$, $\ell$ cannot depend on $c_s$ and obtains according to eq. (2) as $\ell = l/\varphi$. However, when $c_s$ increases above a threshold concentration $c^*_s(\varphi)$, VAN DER WAALS attractions start being dominant in the sense that the virial coefficient $\chi(c_s)$ becomes larger than the swelling limit line $\chi(\varphi)$ drawn in fig. 8. For the same given overall composition $\varphi$, the swollen stack of GO sheets phase-separates, part of the volume being filled with pure solvent ($\varphi_t = 0$), a more concentrated GO–solvent system with $\varphi_t \geq \varphi$ occupying the remaining volume–left- and right-end of dashed binodals in fig. 8

Since $\ell$ remains equal to $l/\varphi$, in the swollen stack, the observed stacking period starts decreasing. Because the swelling limit line $\chi(\varphi)$ in fig. 8 increases with $\varphi$, the phase separation phenomenon occurs earlier (i.e. for a lower salt content) if the lamellar stack is initially more dilute.

To proceed further in quantitative terms, it would be desirable to directly measure the properties controlling the swelling behaviour in GO stacks, viz. the bending modulus $\kappa$ of the GO sheet and the sheet–sheet interaction potential or, at least, the MILNER–ROUX virial coefficient $\chi$ [25], in particular as a function of $c_s$. As an intermediate step before reaching this ultimate goal, we propose below a method (based upon a model description of the small-angle x-ray–or neutron–diffractograms) for estimating the CAILLÈ exponent $\eta$. This parameter was originally introduced for describing elastic fluctuations in smectic A liquid crystals [50–52] and is related to both smectic layer flexibility and interactions. It also proved useful in interpreting characteristic features of diffractograms of lyotropic lamellar $L_\alpha$ phases see, e.g., [35,44,45,51], as well as of GO stacks [6].

The intensity $I$ of the radiation scattered by unoriented ("powder") lamellar samples can be shown to a good approximation to be proportional to the product of two main terms [35-53]

$$I(q) = A \frac{2\pi}{q^2} P(q) S(q)$$

(6)

where $P$ and $S$ are, respectively, the form and structure factors, accounting for the scattering along their normal by isolated flat "particles" and, along the stacking axis, by a 1D periodic structure. In eq. (6), $q$ is the magnitude of the scattering wave vector and $A$ is a normalising constant that depends on "particle”–solvent contrast, composition, etc. The $1/q^2$ term accounts at large enough wave vectors for the powder average [55], and can also be considered as the "particle” in-plane form factor $S$.

With the further simplification of considering the GO sheets as zero-thickness "particles", the form factor $P$ no longer depends on $q$ and remains equal to 1, an acceptable approximation in the investigated SAXS range. On the other hand, the structure factor is conveniently expressed as results from the following equations (7) and (8)

$$S(q) = 1 + 2 \sum_{n=1}^{N-1} \left(1 - \frac{n}{N}\right) \times \cos \left[\frac{q\ell n}{1 + 2\Delta q^2\ell^2 \alpha(n)} \right] \times \frac{\exp \left\{ -2q^2\ell^2 \alpha(n) + \Delta q^2\ell^2 \alpha(n) \right\}}{\sqrt{1 + 2\Delta q^2\ell^2 \alpha(n)}}$$

(7)

$$\alpha(n) = \frac{\eta}{4\pi^2} \left[ \log (\pi n) + \gamma \right]$$

(8)

where $N$ is the number of correlated GO sheets in the lamellar stack, $\ell$ the period of the structure, $\Delta q$ the Gaussian width of the resolution (or FWHM/\sqrt{8 \ln 2}) and $\gamma \approx$
0.57721… the value of Euler’s constant \( e \). Note that owing to the logarithmic term in eq. (3), characteristic of the anomalous fluctuation properties in one-dimensional systems [50–52], the structure factor given in eq. (7) differs essentially from the results relevant for the so-called disorders of the first or second kinds, or para-crystalline theory—see, e.g., [53].

The model, though being somehow equivocal because the resolution of our experiment is limited, the distinction between (small) \( N \) and (large) \( \eta \) roles therefore becoming less clear-cut in some cases, has nevertheless been used to tentatively describe the diffractograms for some rather disorders of the first or second kinds, or para-crystalline defects essentially from the results relevant for the so-called disorders of the first or second kinds, or para-crystalline theory—see, e.g., [53].

Figure 9 displays two results, and fitting parameters are given in table 1.

![SAXS spectra in the Kratky representation for a GO dispersion in pure water (σ). The full line is the best fit of eq. (2) to the data. Inset: \( f_m = 4.3 \% \) system (τ)](image)

**Table 1. Model parameters**

| Parameter | \( f_m = 0.014 \) | \( f_m = 0.028 \) | \( f_m = 0.043 \) | \( f_m = 0.071 \) |
|-----------|----------------|----------------|----------------|----------------|
| \( ℓ \) [nm] | 42.7 | 23.8 | 17.4 | 10.2 |
| \( \eta \) | 0.39 | 0.75 | 0.65 | 0.93 |
| \( N \) | 20 | 10 | 10 | 7 |

A fair description of the small-angle scattering features is obtained when using the proposed model, with nevertheless obvious shortcomings for scattering wave vectors in the range \( 0.08 - 0.16 \) \( \text{Å}^{-1} \) that may result from the crudeness of our assumption as regards the GO sheet form factor. In particular, the dangling oxygen-rich groups present in GO sheets may increase locally the sheet thickness, therefore contributing to out-of-plane features of the form factor not accounted for in our simplified description.

From the fitted values of the CAILLÉ exponent \( \eta \), the smectic compression modulus \( B \) of the lamellar structure made of stacked GO sheets may be estimated. With

\[
\eta = \frac{\eta_B^2 k_B T}{8\pi \sqrt{KB}}
\]

from ref. [50], and using for the smectic splay modulus \( K \) the relation \( K = \kappa/\ell^2 \) [26], we get

\[
\frac{\ell^3 B}{k_B T} = \frac{\pi^2 k_B T}{4 \kappa \eta^2}
\]

or \( B \approx 6 \) for \( f_m = 4.3 \% \) (respectively, \( B \approx 16 \) for \( f_m = 1.4 \% \)) in \( k_B T/\ell^3 \) units if, as proposed in ref. [43], the value of the GO sheet bending modulus \( \kappa \) is actually equal to \( k_B T \). Such values for the smectic compression modulus \( B \), significantly larger than predicted in the HELFRICH model, namely \( \ell^3 B_H/(k_B T) = 9\pi^2 k_B T/(64\kappa) \) [26] (or \( \approx 1.4 \) in \( k_B T/\ell^3 \) units), are quite reasonable in the presence of dominantly repulsive interactions between GO sheets. Indeed, from MILNER-ROUX analysis of the “un-binding” transition [28], the smectic compression modulus \( B \) should be expressed as [44]

\[
\frac{\ell^3 B}{k_B T} = \frac{9\pi^2 k_B T}{64\kappa(1 - t/t')^4} - 2\chi t^2
\]

which, from eq. (10) with \( \ell \) and \( \eta \) values as given in table 1, yields roughly the same estimate for the virial coefficient \( \chi t^3 \approx -0.04 \) for the two GO concentrations, with a negative sign as expected for overall repulsive interactions.

The structural phase transition that occurs in the vicinity of \( \ell = 2.5 \text{ nm} \) is actually also amenable, qualitatively at least, to an interpretation in terms of MILNER-ROUX arguments. As shown in fig. 10, the CAILLÉ exponent is expected to strongly increase when the lamellar stack of...
GO sheets is dehydrated, until a characteristic period $t^\ast$ is reached beyond which $\eta$ decreases to very small values. As larger $\eta$ values are associated to (lamellar) Bragg peaks with lesser peak intensities and broader tails, the quasi-disappearance of the first and second order Bragg peaks in a given dilution range (see fig. 5) may thus be understood, even though the predicted $t^\ast$ value, namely 5.4 nm, clearly differs from its experimental counterpart. However, since the Milner-Roux description of the unbinding transition is a mean-field, perturbative theory, we believe that such a discrepancy should not be too seriously deplored for such concentration ranges where direct interactions between GO sheets are definitely strong.

4 Conclusion

A procedure to concentrate aqueous GO dispersions to significant dryness, with the benefit of avoiding the formation of aggregates has been implemented. The lamellar stacks of GO sheets obtained in an extended concentration range, from ca. 2 % to 72 %, can be reversibly swollen or dehydrated. The simple one-dimensional dilution law is largely obeyed over all the investigated hydration range, even though conspicuous discrepancies have been revealed by small-angle x-ray scattering studies that may indicate the occurrence of an underlying, as yet unidentified, structural phase transition.

The swelling behaviour of the aqueous GO dispersions can be interpreted, similarly to many lyotropic lamellar L$_\alpha$ phases in amphiphilic systems, in terms of an entropic “force” arising from the confinement of undulation fluctuations (also known as Helfrich undulation interactions) acting together, or competing with, direct forces, respectively electrostatic repulsions and van der Waals attractions. The so-called “unbinding transition” mechanism appears here to be mainly driven by the ionic strength of the aqueous medium swelling the GO sheets, as indirectly suggested by the quantitative analysis of the small-angle x-ray diffractograms in terms of a parameter, the Caille exponent $\ell$, that combines the bending and compression moduli characterising the elastic properties of lamellar phases. The analysis confirms the recently proposed “super-flexible” nature of GO sheets.[31]

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Figures have been drawn with the 2D graphics package Matplotlib.[56]

5 Author contribution statement

L.N., and F.N. conceived and planned the research. R.L.R. conceived and implemented the drying procedure. R.L.R., M.A.B., T.M., and K.B. contributed to sample preparation and carried out the experiments. All authors provided critical feedback and helped shape the research, analysis and manuscript. All the authors have read and approved the final manuscript.

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