Three-dimensional Orientation of Nanofibrils in Axially Symmetric Systems using Small Angle X-ray Scattering

Tomas Rosén,^{*,†,‡,¶} Christophe Brouzet,^{†,‡} Stephan V. Roth,^{§,||} Fredrik Lundell,^{†,‡}
and L. Daniel Söderberg^{†,‡}

[†]*Linné FLOW Centre, KTH Mechanics, Royal Institute of Technology, SE-100 44
Stockholm, Sweden*

[‡]*Wallenberg Wood Science Center, Royal Institute of Technology, SE-100 44 Stockholm,
Sweden*

[¶]*Present address: Department of Chemistry, Stony Brook University, Stony Brook, NY
11794-3400, USA*

[§]*DESY, Notkestrasse 85, Hamburg, Germany*

^{||}*Department of Fibre and Polymer Technology, Teknikringen 56-58, Royal Institute of
Technology, SE-100 44 Stockholm, Sweden*

E-mail: rosen@mech.kth.se

Abstract

The increased availability and brilliance of new X-ray facilities have in the recent years opened up the possibility to characterize the alignment of dispersed anisotropic nanoparticles in various microfluidic applications, from hydrodynamic self assemblies to flows in complex geometries. In such applications, it is vital to study the alignment of the nanoparticles in the flow, as this in turn affects the final properties of the self-assembled superstructures or those of the flow itself. Small angle X-ray scattering (SAXS) is a well-suited characterization technique for this, but typically provides the alignment in a projected plane perpendicular to the beam direction. In this work, we demonstrate a simple method to reconstruct the full three-dimensional (3D) orientation distribution function (ODF) from a SAXS-experiment through the assumption that the azimuthal angle of the nanoparticles around the flow direction is distributed uniformly; an assumption that is valid for a large range of nanoparticle flow processes. For demonstration purposes, the experimental results from previous works on hydrodynamic self-assembly of cellulose nanofibrils (CNF) into filaments have been revised, resulting in a small correction to the presented order parameters. The results are then directly compared with simple numerical models to describe the increased alignment of CNF both in the flowing system and during the drying of the filament. The proposed reconstruction method will allow for further improvements of theoretical or numerical simulations and consequently open up new possibilities for optimizing assembly processes, which include flow-alignment of elongated nanoparticles.

1. Introduction

Studying the alignment of anisotropic nanoparticles or polymers in flows is relevant in many applications, for example in fibre spinning¹ or creating nanostructured films.^{2,3} In many of these material processes, the particle shapes and orientations will have a significant effect on macroscopic properties. For example, the macroscopic electrical response of films made from carbon nanotubes is greatly affected by the alignment of the nanoparticles inside the

material.⁴⁻⁸ Other applications relate to the influence of the orientation on macroscopic optical properties of the material such as its refractive index.³

The orientation distribution of the anisotropic nanoparticles inside the material is often dependent on their dynamics in a flowing dispersed state in the process. Therefore it is of great importance to understand how the angular dynamics and alignment of nanoparticles in flows can be studied, modeled and controlled during the processing of materials.

The description of the particle orientation in the flow is usually through spherical coordinates with polar angle ϕ between the particle major axis and the flow (z) direction, and the azimuthal angle θ in the plane perpendicular to the flow (see figure 1a-b). Here, the viewing direction is the negative y -direction, such that the viewing plane is equal to the xz -plane.

Figure 1: (a) Definition of the orientation of an elongated particle with unit vector $\mathbf{p}$ along the major axis; the polar angle of the particle to the z -direction is denoted with ϕ and the corresponding azimuthal angle in the xy -plane is θ ; the projection of the unit vector $\mathbf{p}$ on the viewing (xz) plane is denoted $\mathbf{p}'$ and has the angle χ with respect to the z -axis; (b) illustration of a flow in a typical experiment; the flow is in z -direction, the viewing direction is defined in negative y -direction; (c) a typical projection of the elongated particles in the viewing plane; (d) schematic illustration of a typical SAXS experiment.

In that plane we define the particle orientation with the projected angle χ . As seen in the figure, these angles are related through

$$\tan \chi = \tan \phi \cos \theta. \quad (1)$$

The nanometer-sized particles of interest are smaller than the visible wavelength of light, and the understanding of their shape and properties must rely on using other characterization techniques than standard microscopy. In solid material, there is the possibility to use highly magnified scanning/transmission electron microscopy (SEM/TEM) images or atomic force microscopy (AFM).⁹ However, to present any statistically relevant orientation distribution function (ODF) describing the collective orientation of particles would require a substantial amount of images being analyzed. Furthermore, we will only obtain the projected angle χ on the viewing plane from these images (see figure 1c) unless the nanoparticles are mono-dispersed and the out-of-plane orientation can be found through the length of the projected particle. Due to the nature of the techniques, neither SEM nor AFM are suitable for studying flowing systems of dispersed nanoparticles.

Following the increased availability and performance of synchrotron light sources, small angle X-ray scattering (SAXS) has proven to be a vital tool for nanoparticle characterization in flowing dispersions.^{10–12} With this technique, the light scattered by the particles is recorded on a detector and this information will describe the shape and size of the particles in an isotropic system (see figure 1d). If the particles are non-spherical and show some preferential alignment, the technique will also provide a statistically relevant ODF.¹³ However, when using SAXS in a transmission geometry, it is important to take into consideration that the experiment just provides the distribution of the projected angle χ . Furthermore, the ODF of the polar angle ϕ is not easy to obtain from the projected distribution of χ . This particular issue will result in a non-trivial comparison between experiments and simulations when it comes to describing the angular dynamics of nanoparticles in flows. To obtain the

three-dimensional ODF with SAXS, the typical approach is by rotating the sample and thus obtaining the projected ODF from different incidence angles from which the three-dimensional orientation can be reconstructed during post-processing.^{14–17} However, such approach is complex, involves a large amount of data and is not easily applicable for flow systems.

If the system has an axial symmetry, i.e. all the particles are in average aligned along a main direction, it is possible to obtain the 3D ODF without rotating the sample. Vainio et al.¹⁸ were able to recover the three-dimensional orientation of carbon nanotubes by fitting the projected ODF using a general normal distribution (GND) function with two parameters. These two parameters characterize the width and the sharpness of the ODF. Assuming axial symmetry, they are mathematically related to the two parameters of the generalized normal distribution function describing the 3D ODF, allowing to recover it.

In this work, in the case of axial symmetry, we propose a new method based on Legendre decomposition of the projected ODF in order to obtain the 3D ODF. This method does not rely on fitting the measured ODF and therefore is applicable on any ODF. Moreover, this method allows us to directly extract the main order parameters of the system, i.e. the physical relevant quantities characterizing the orientation of the particles. This paper has the following outline. Firstly, some methodology information are provided to the reader regarding some basics on the study of the angular dynamics of dispersed nanofibrils both numerically and experimentally using SAXS. In the following sections, this new Legendre decomposition method is presented and validated using simulated ODF. The method is finally applied to previous works performed by Håkansson et al.^{19,20}, allowing a quantitative comparison with simple physical models.

2. Methodology

2.1. Cellulose filament fabrication as a test case

As the studies performed by Håkansson et al.^{19, 20} are used in this paper to demonstrate our method, we quickly recall to the reader the main findings that are needed in the following. Using a dispersion of cellulose nanofibrils (CNF), Håkansson et al.¹⁹ exhibited a process of making strong and stiff cellulose filaments that could potentially be used in new biobased composites or high performance textiles. Indeed, structural materials in nature are found to have properties that can surpass the performance of their individual components,²¹ and thus offer great potential to meet the demands of a sustainable society. Using biobased nanoparticles as building blocks, there have recently been several other examples of using flow alignment to control the assembly of new types of materials and composites.^{22–24} The filament process by Håkansson et al.¹⁹ is schematically illustrated in figures 2a-c. In a flow-focusing device, a dispersion of CNF is focused by a sheath flow of a NaCl solution. During the acceleration of the core flow, the fibrils are hydrodynamically aligned in the flow direction

Figure 2: Demonstration of the flow-focusing device and the process to make strong cellulose filaments from CNF through the method by Håkansson et al.¹⁹; (a) the flow-focusing device with a core flow of a CNF suspension and sheath flows containing salt and water; (b) the filament production consists of three steps: (I) hydrodynamic alignment of CNF in the z -direction, (II) transition of the CNF from a dispersion to an arrested (gel) state, (III) drying of the gel-thread; (c) SEM image of the final dried cellulose filament with the black scale bar indicating $20\ \mu\text{m}$; figures (a) and (c) are adapted from Håkansson et al.¹⁹.

almost solely due to extensional flow. As the ions in the sheath flow are diffusing into the core, the CNF is forming a gel where the internal structure of fibrils are locked in an aligned state. After a subsequent drying of the gel thread believed to cause further alignment, a continuous filament is produced with strength and stiffness that could potentially be comparable to glass fibers. The mechanical properties of the resulting filament were seen to be dependent on the degree of alignment of CNF along the filament direction. Increasing the alignment of CNF in the flow-focusing process could thus potentially lead to an even stronger material.

The alignment of the CNF in the flow was studied by Håkansson et al.¹⁹ using SAXS by quantifying the anisotropy in the scattering pattern. In a later work, Håkansson et al.²⁰ demonstrated how the evolution of the ODF of particles in the flow-focusing device can be simulated. The simulated alignment based on the polar angle ϕ was then compared with the alignment based on the projected angle χ in the SAXS patterns in a simplified manner. In addition, Håkansson et al.¹⁹ characterized the alignment of the nanofibrils in the dried filament with wide angle X-ray scattering (WAXS), relying on the same principle as SAXS. This means that the mean fibril angle obtained in this study also represents the mean projected angle $\langle\chi\rangle$ and not the mean polar angle $\langle\phi\rangle$ to the fiber direction.

2.2. Quantifying alignment

The probability of a fibril to have an orientation in the interval $\phi \in [\phi_1, \phi_2]$ and $\theta \in [\theta_1, \theta_2]$ is given by the following expression using the ODFs Ψ_ϕ and Ψ_θ

$$\text{Pr}[\phi_1 \leq \phi \leq \phi_2, \theta_1 \leq \theta \leq \theta_2] = \int_{\theta_1}^{\theta_2} \Psi_\theta d\theta \int_{\phi_1}^{\phi_2} \Psi_\phi |\sin \phi| d\phi, \quad (2)$$

where the two functions are normalized according to

$$2\pi \int_{-\pi/2}^{\pi/2} \Psi_\phi |\sin \phi| d\phi = 1 \quad \text{and} \quad \frac{1}{2\pi} \int_0^{2\pi} \Psi_\theta d\theta = 1. \quad (3)$$

Throughout this work, axial symmetry is assumed meaning that the azimuthal angle θ

is distributed uniformly, i.e. $\Psi_\theta = 1$.

To describe the collective alignment of many elongated particles in the flow, the mean of the second Legendre polynomial $S_\phi = \langle P_2(\cos \phi) \rangle$ is commonly used and sometimes called *Hermans order parameter*. This quantity is expressed as:²⁵

$$S_\phi = \langle P_2(\cos \phi) \rangle = \left\langle \frac{3}{2} \cos^2 \phi - \frac{1}{2} \right\rangle, \quad (4)$$

where the brackets denote an ensemble average over all particles. Consequently, $S_\phi = 0$ if all particles are uniformly distributed and $S_\phi = 1$ if the particles are perfectly aligned in the flow direction. Using the ODF Ψ_ϕ , the order parameter S_ϕ can be obtained through

$$S_\phi = \int_0^{2\pi} d\theta \int_{-\pi/2}^{\pi/2} \Psi_\phi \left(\frac{3}{2} \cos^2 \phi - \frac{1}{2} \right) |\sin \phi| d\phi. \quad (5)$$

Additionally, it should be mentioned that the value of S_ϕ might not always be a good measure of the true ODF Ψ_ϕ since it corresponds to an integrated quantity. This means of course that different ODFs can correspond to the same order parameter. For example, an order parameter of $S_\phi = 0$ could both mean that the system is isotropic, but could also mean that all fibers are perfectly oriented at an angle of $\phi = \arccos \sqrt{1/3} \approx 54.7^\circ$. It is therefore necessary to have access to the full ODF, by SAXS measurements or numerical simulations.

2.3. Dynamics of small particles in flows

The dynamics of small particles in flows can be modelled using a Smoluchowski equation. The details about the derivation of this model along with improvements to account for interacting fibrils are given by Doi and Edwards²⁶ and Håkansson et al.²⁰. In the flow-focusing process illustrated in figure 2, it is reasonable to assume that the core flow of CNF is only in the z -direction and the velocity $\mathbf{u} = (u, v, w)$ does not vary in the radial direction, i.e. $u = v = 0$.²⁰ This means that Ψ_θ always will remain constant and Ψ_ϕ will only be dependent on the centerline velocity $w_c = w_c(z)$, the extension rate $\dot{\epsilon} = \dot{\epsilon}(z) = dw_c/dz$ and

the rotary diffusion coefficient D_r . Assuming that the dispersion is dilute and the fibrils do not interact with each other and further assuming that the fibrils can be described as stiff spheroids with aspect ratio r_p (major axis/minor axis), the steady state of $\Psi_\phi = \Psi_\phi(z)$ is given by the Smoluchowski equation^{20,26}

$$w_c \frac{\partial \Psi_\phi}{\partial z} = \frac{1}{\sin \phi} \frac{\partial}{\partial \phi} \left(\underbrace{D_r \sin \phi \frac{\partial \Psi_\phi}{\partial \phi}}_{\text{rotary diffusion}} - \underbrace{\sin \phi \frac{\partial \phi}{\partial t} \Psi_\phi}_{\text{hydrodynamic forcing}} \right), \quad (6)$$

where the angular velocity is determined by Jeffery²⁷ as:

$$\frac{\partial \phi}{\partial t} = -\dot{\epsilon} \Lambda \frac{3}{2} \cos \phi \sin \phi \quad (7)$$

with

$$\Lambda = \frac{r_p^2 - 1}{r_p^2 + 1}. \quad (8)$$

The assumptions made to justify this particular model are of course very questionable for the actual flow of CNF under process-relevant conditions, but will be used in this work only for the sake of discussion.

The Smoluchowski equation above is only dependent on one dimensionless parameter, called the Péclet number Pe and is defined as:

$$Pe = \frac{\dot{\epsilon} \Lambda}{D_r}, \quad (9)$$

which relates the effect of hydrodynamic forcing with the effect of Brownian rotary diffusion. For example, if $Pe = \infty$, the rotary diffusion term can be neglected in eq. (6). Analogously, if $Pe = 0$, the hydrodynamic forcing term can be neglected. For a constant value of Pe (constant extension rate and rotary diffusion), there will be an equilibrium distribution given by the solution of $d\Psi_\phi/dz = 0$. The equilibrium distribution can be analytically found

to be (see supplementary information for full derivation):

$$\Psi_{\phi}^{\text{eq}} = \frac{\exp(-\frac{\sin^2 \phi}{2\sigma^2})}{\int_0^{2\pi} d\theta \int_{-\pi/2}^{\pi/2} \exp(-\frac{\sin^2 \phi}{2\sigma^2}) |\sin \phi| d\phi}, \quad (10)$$

with

$$\sigma^2 = \frac{2}{3Pe}. \quad (11)$$

2.4. Small Angle X-ray Scattering (SAXS)

The typical setup for a transmission SAXS experiment used by Håkansson et al.¹⁹ to study the alignment of nanofibrils in a flow was illustrated previously in figure 1d. The X-ray beam with wavelength λ is illuminating the flowing dispersion in the negative y -direction, perpendicular to the flow (z) direction. Some of the incoming photons are scattered by the particles and the scattered light is a representation in the reciprocal space of the illuminated fibrils. The scattered light intensity I is collected on a detector placed at a distance D from

Figure 3: (a) A **schematic** illustration of the scattering intensity on the detector in a SAXS experiment; (b) the averaged ODF Ψ_χ obtained from the SAXS experiments by Håkansson et al.¹⁹ in the flow-focusing device at $z = 2.5h$; the blue curve shows the ODF Ψ_χ normalized using eq. (12) and is denoted $\Psi_\chi^{(2D)}$ while the red curve shows the ODF normalized with eq. (13) and is denoted $\Psi_\chi^{(3D)}$.

the sample. A schematic illustration of the X-ray scattering intensity on the detector is given in figure 3a. The anisotropy in the SAXS pattern, with higher scattering intensity in the x -direction, reflects the fact that the sample is preferentially oriented in the z -direction. After subtraction of the background scattering intensity as well as the scattering contribution from the length of the particle, the normalized intensity along a constant $q = (4\pi/\lambda) \sin \varphi$ provides an estimate of the ODF Ψ_χ of the projected fibril angle χ . The typical ODF is furthermore averaged in a q -range corresponding to length scales between the typical width W and length L of the fibrils, i.e. $q \in [2\pi/L, 2\pi/W]$. If the aspect ratio of the nanofibrils is low, the ODF is more difficult to extract from SAXS as a significant part of the scattering pattern will be attributed to the length of the particles, which means that the relative intensity of the oriented part of the scattering pattern is lower. Furthermore, the q -range over which the averaging is done will be small, leading to questionable statistics. Practically, the technique is thus primarily suitable for nanofibril systems with high aspect ratios ($L \gg W$), which is also the case in most material processes where the orientation distribution is important, e.g. materials from CNF, carbon nanotubes etc.

Typically, there are two ways often used to normalize the function Ψ_χ . Either the angle χ is treated as an azimuthal angle in a 2D plane and is thus normalized according to

$$\int_{-\pi/2}^{\pi/2} \Psi_\chi^{(2D)} d\chi = 1, \quad (12)$$

or the angle χ is treated as a representation of the polar angle in 3D space and thus normalized according to

$$\int_0^{2\pi} d\theta \int_{-\pi/2}^{\pi/2} \Psi_\chi^{(3D)} |\sin \chi| d\chi = 1. \quad (13)$$

The two distributions $\Psi_\chi^{(3D)}$ and $\Psi_\chi^{(2D)}$ are only differing with a constant scaling factor α such that $\Psi_\chi^{(3D)} = \alpha \Psi_\chi^{(2D)}$ with

$$\alpha = \left(\int_0^{2\pi} d\theta \int_{-\pi/2}^{\pi/2} \Psi_\chi^{(2D)} |\sin \chi| d\chi \right)^{-1}. \quad (14)$$

An illustration showing the difference in scaling of Ψ_χ is illustrated in figure 3b.

In the work by Håkansson et al.¹⁹, the order parameter obtained from the SAXS experiments is found by using the 3D normalization of Ψ_χ according to

$$S_\chi = \int_0^{2\pi} d\theta \int_{-\pi/2}^{\pi/2} \Psi_\chi^{(3D)} \left(\frac{3}{2} \cos^2 \chi - \frac{1}{2} \right) |\sin \chi| d\chi. \quad (15)$$

Given this definition, S_χ is also equal to zero when the particles have an isotropic orientation distribution and $S_\chi = 1$ if the particles are perfectly aligned in z -direction. However, for an arbitrary orientation distribution the two order parameters S_χ (based on the projected angle χ) and S_ϕ (based on the polar angle ϕ) are not the same.

3. Results and Discussions

3.1. Reconstructing Ψ_ϕ from Ψ_χ

The SAXS experiments give us access to the projected ODF Ψ_χ of the ODF Ψ_ϕ . Depending on normalization of Ψ_χ according to eqs. (12) and (13), the ODFs $\Psi_\chi^{(2D)}$ and $\Psi_\chi^{(3D)}$ can be obtained. To be able to reconstruct Ψ_ϕ from Ψ_χ , we can use the different symmetries of the system. We assume here that the ODF is axi-symmetric around the flow axis z , meaning that the ODF depends only on ϕ and not on θ . Following Van Gurp²⁵, the ODF Ψ_ϕ can be expressed as a series expansion of Legendre polynomials:

$$\Psi_\phi = \sum_{j=0,2,4,\dots}^{2(N_{LP}-1)} \frac{2j+1}{4\pi} \langle P_j \rangle_\phi P_j(\cos \phi), \quad (16)$$

where P_j is the Legendre polynomial of order j and $\langle P_j \rangle_\phi = \langle P_j(\cos \phi) \rangle$ is the j -th order parameter of the ODF. The exact result is obtained as $N_{LP} \rightarrow \infty$. Note that S_ϕ corresponds to the second order parameter $\langle P_2 \rangle_\phi$. Here, we use only the even Legendre polynomials because the ODF follows the symmetry condition $\Psi_\phi(\phi) = \Psi_\phi(\pi - \phi)$.

In the same way, the projected ODF using the 3D normalization can also be decomposed in Legendre polynomials:

$$\Psi_{\chi}^{(3D)} = \sum_{i=0,2,4,\dots}^{2(N_{LP}-1)} \frac{2i+1}{4\pi} \langle P_i \rangle_{\chi} P_i(\cos \chi), \quad (17)$$

with $\langle P_i \rangle_{\chi} = \langle P_i(\cos \chi) \rangle$.

The order parameters $\langle P_j \rangle_{\phi}$ and $\langle P_i \rangle_{\chi}$ are related through (see derivation in supplementary information)

$$\begin{pmatrix} \langle P_0 \rangle_{\chi} \\ \langle P_2 \rangle_{\chi} \\ \vdots \\ \langle P_N \rangle_{\chi} \end{pmatrix} = \frac{\alpha}{2} \begin{pmatrix} C_{0,0} & C_{0,2} & \dots & C_{0,N} \\ C_{2,0} & C_{2,2} & \dots & C_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ C_{N,0} & C_{N,2} & \dots & C_{N,N} \end{pmatrix} \begin{pmatrix} \langle P_0 \rangle_{\phi} \\ 5\langle P_2 \rangle_{\phi} \\ \vdots \\ (2N+1)\langle P_N \rangle_{\phi} \end{pmatrix} \quad (18)$$

with $N = 2(N_{LP} - 1)$ and the $N_{LP} \times N_{LP}$ matrix $C_{i,j}$ given by

$$C_{i,j} = \int_{-\pi/2}^{\pi/2} P_i(\cos \chi) |\sin \chi| \left(\int_0^1 \frac{4p'}{\sqrt{1-p'^2}} P_j(p' \cos \chi) dp' \right) d\chi, \quad (19)$$

for $i, j = 0, 2, 4 \dots 2(N_{LP} - 1)$. Note here that the matrix $C_{i,j}$ does not depend on the actual ODF, and can be pre-computed for a given N_{LP} .

Now, the ODF Ψ_{ϕ} based on the polar angle can be reconstructed from the projected ODF Ψ_{χ} using the following steps:

1. Normalize Ψ_{χ} in two ways according to eqs. (12) and (13) to obtain $\Psi_{\chi}^{(2D)}$, $\Psi_{\chi}^{(3D)}$ and α .
2. Find the order parameters $\langle P_i \rangle_{\chi}$ using

$$\langle P_i \rangle_{\chi} = \int_0^{2\pi} d\theta \int_{-\pi/2}^{\pi/2} \Psi_{\chi}^{(3D)} P_i(\cos \chi) |\sin \chi| d\chi \quad (20)$$

3. Compute the matrix $C_{i,j}$ for the N_{LP} first even Legendre polynomials using eq. (19).

The exact analytical values of the matrix $C_{i,j}$ for $N_{LP} \leq 15$ is given as a separate file in the online supplementary material.

4. Inverse eq. (18) to obtain the order parameters $\langle P_j \rangle_\phi$.
5. Reconstruct Ψ_ϕ using eq. (16).

A method for comparing ODFs and taking into account the projected orientation was also proposed by Vainio et al.¹⁸. The projected ODF Ψ_χ was fitted to a generalized normal distribution (GND) with two fitting parameters describing the shape of the ODF and allowing the 3D-ODF Ψ_ϕ to be recovered. There are however several advantages with the present Legendre-method compared to the GND fitting method by Vainio et al.¹⁸:

1. The Legendre-method can decompose any projected ODF while the GND fitting method is limited to a certain type of projected ODF, even if the shape can be rather general with the help of the two fitting parameters.
2. The description of the 2D ODFs with Legendre polynomials is only done with even powers of $\cos \chi$. This means that the resulting function is automatically cyclic in the range $\chi \in [-\pi/2, \pi/2]$. The GND function is not cyclic and is therefore not suitable for weakly aligned systems where the ODF at $|\chi| = \pi/2$ is substantially larger than zero.
3. The Legendre-method automatically uses Hermans orientation factor $\langle P_2 \rangle_\chi$ as one of the comparable parameters, which is already widely used as a measurement of ODF alignment.
4. The Legendre-method is not a fitting method. The parameters obtained independently are the coefficients of orthogonal polynomials and are all order parameters of the system. For example, the parameter $\langle P_4 \rangle_\chi$ is a mathematical property of the underlying data just like Hermans orientation factor $\langle P_2 \rangle_\chi$. In a regular fitting process, the fitting parameters cannot be obtained independently from each other.

3.2. Validation of the reconstruction method

To demonstrate the validity of the reconstruction, three different physical processes are numerically simulated in order to describe typical distributions of Ψ_ϕ that we can encounter in a flow of nanoparticles:

1. *Uni-axial extensional flow.* The system of isotropically distributed particles at $z = 0$ is stretched with a uni-axial extensional flow without any influence of rotary diffusion ($Pe = \infty$) until almost fully aligned at some downstream position z . On the centerline, there is thus a constant acceleration and the velocity is given by $w_c = \dot{\epsilon}z$, with $\dot{\epsilon}$ as an arbitrary constant extension rate and the alignment increases with z .
2. *Rotary diffusion.* An almost fully aligned system of particles at $z = 0$ is subject to rotary diffusion without any hydrodynamic forcing ($Pe = 0$). On the centerline, there is thus no acceleration and the velocity is given by $w_c = w_0$ with w_0 as an arbitrary constant velocity. The alignment will then decrease with z .
3. *Equilibrium.* Given various constant $Pe \in]0, \infty[$, a system of isotropically distributed particles at $z = 0$ is subject to a flow with constant acceleration ($w_c = \dot{\epsilon}z$). Far downstream, as $z \rightarrow \infty$, the system will reach the equilibrium distribution given by the steady state solution Ψ_ϕ^{eq} given in eq. (10).

In the cases 1 and 2, the ODF at a given downstream position $\Psi_\phi(z)$ is provided by numerically integrating the Smoluchowski equation (eq. (6)) in Matlab R2013b. For case 3, the equilibrium ODF Ψ_ϕ^{eq} is given directly by eq. (10) for various Pe . The azimuthal angle θ is distributed uniformly, i.e. $\Psi_\theta = 1$.

Given these ODFs, Monte-Carlo simulations were performed in Matlab R2013b. A total of $N = 10^7$ particles are sampled, and for each particle, the orientation (ϕ, θ) is randomly chosen from the distributions Ψ_ϕ and Ψ_θ . For each particle, the projected angle χ is subsequently calculated through eq. (1), which is used to obtain the distribution Ψ_χ numerically. An

Figure 4: Histogram for $N = 10^7$ particles illustrated with the gray area; (a) the ODF Ψ_ϕ obtained from the Smoluchowski simulations with uni-axial extension and no rotary diffusion at $S_\phi = 0.30$; (b) the angle θ is sampled from a uniform distribution; (c) the resulting ODF $\Psi_\chi^{(3D)}$ with a projected order parameter of $S_\chi = 0.19$; the curves in (a) and (c) correspond to the reconstruction of Ψ_ϕ for given N_{LP} of Legendre polynomials used to fit $\Psi_\chi^{(3D)}$ in (c).

example is shown in figure 4. The distribution Ψ_ϕ in figure 4a is obtained from the simulation of the uni-axially extended system without diffusion at $S_\phi = 0.3$. In order to account for the correct probability on the unit sphere, the distribution is multiplied with $|\sin \phi|$ and random numbers are generated from the distribution $\Psi_\phi |\sin \phi|$ to form the histogram in figure 4a. Figure 4b shows the histogram of the uniformly distributed values of θ and figure 4c shows the corresponding histogram of the projected angle χ for all the particles, where the distribution is normalized according to eq. (13) to form the ODF $\Psi_\chi^{(3D)}$. The distribution $\Psi_\chi^{(3D)}$ is then used as an input for the reconstruction method described previously. As seen in figure 4a, the proposed method manages to almost perfectly recover the initial distribution of Ψ_ϕ when utilizing at least $N_{LP} = 6$ Legendre polynomials.

In figure 5, it is observed how the order parameter S_ϕ will differ from the measured projected order parameter S_χ . The discrepancy is larger during the acceleration of the flow when uni-axial extension is dominating, while approaching almost a one-to-one correspondence when Brownian rotary diffusion is dominating. Regardless of which type of distributions we encounter, we find that the proposed reconstruction manages to almost exactly recover Ψ_ϕ from Ψ_χ with $N_{LP} = 10$ (cross symbols in figure 5). For the highly aligned

Figure 5: Illustration of how the measured projected order parameter S_χ differs from the true order parameter S_ϕ given the different flowing processes described in the text; the cross symbols denote the results from the reconstruction using $N_{LP} = 10$; the arrow indicates the conditions for which the histograms in figure 4 were drawn.

($S_\phi \gtrsim 0.9$) uni-axially strained system, the reconstruction method is more sensitive and a larger number of Legendre polynomials would be needed. Note here also that $S_\phi \approx 0.9$ when $S_\chi \approx 0.6$. It would thus be very difficult to measure any higher alignment $S_\chi > 0.6$ in a SAXS experiment with a uni-axially extended dispersion. A measured value of $S_\chi \approx 0.6$ is thus actually representing a system that is close to perfect alignment in reality.

3.3. Comparing ODF shapes

The difference seen in the previous section between $S_\phi = \langle P_2 \rangle_\phi$ and $S_\chi = \langle P_2 \rangle_\chi$ comes from the fact that the ODFs have different shapes. In figure 6a, distributions $\Psi_\chi^{(3D)}$ obtained for extensional flow and Brownian rotary diffusion, respectively, are illustrated at approximately the same projected alignment $S_\chi \approx 0.3$. Figure 6b shows the corresponding even Legendre

order parameters $\langle P_i \rangle_\chi$ in log scale for increasing order i . The ODF obtained after extensional flow displays values of $\langle P_i \rangle_\chi$ that decrease more slowly with respect to i than the ODF obtained after Brownian rotary diffusion of a fully aligned system. Essentially, this means that a higher number of Legendre polynomials are needed to accurately represent the ODF, which in turn typically is a consequence of sharper features in the ODF. The projected ODF obtained from the Brownian rotary diffusion process is smoother and does thus not need to be decomposed in higher order Legendre polynomials to be accurately represented. A shape parameter γ for the ODF can be defined as

$$\gamma = \log \left(\frac{\log \langle P_4 \rangle_\chi}{\log \langle P_2 \rangle_\chi} \right) / \log 2, \quad (21)$$

where

$$\langle P_4 \rangle_\chi = \left\langle \frac{1}{8} (35 \cos^4 \chi - 30 \cos^2 \chi + 3) \right\rangle. \quad (22)$$

Figure 6: (a) Comparison between ODFs $\Psi_\chi^{(3D)}$ obtained with uni-axial extensional flow and Brownian rotary diffusion at approximately same degree of alignment given by $S_\chi = \langle P_2 \rangle_\chi \approx 0.3$; the cross symbols show the Legendre reconstruction of the ODFs using $N_{LP} = 6$; (b) Legendre order parameters $\langle P_i \rangle_\chi$ in log scale with respect to i for the ODFs in (a); the thick dashed line shows the order parameters of an ODF with $S_\chi = 0.3$ and $\gamma = 1$.

Figure 7: (a) The ODF $\Psi_{\chi}^{(3D)}$ obtained from SAXS experiments by Håkansson et al.¹⁹ (gray histogram) is fitted with Legendre polynomials using $N_{LP} = 2, 4$ and 15 ; (b) the resulting reconstruction of Ψ_{ϕ} ; (c) the mean square error between the experiment and the model of $\Psi_{\chi}^{(3D)}$ as function of N_{LP} .

The black dashed line in figure 6b represents the order parameters of an ODF with $S_{\chi} = 0.3$ and $\gamma = 1$. The threshold value $\gamma = 1$ actually corresponds to an exponential decay of the order parameters $\langle P_i \rangle_{\chi}$ as a function of the number of Legendre polynomials i . This threshold separates well the ODF obtained from extensional flow ($\gamma \leq 1$) and the one obtained after Brownian rotary diffusion ($\gamma \geq 1$). The parameters $S_{\chi} = \langle P_2 \rangle_{\chi}$ and γ can consequently be used to compare the alignment and shape of different measured anisotropic ODFs ($S_{\chi} \gtrsim 0.1$) of the projected angle χ , even in situations where axial symmetry is not valid.

3.4. Application to SAXS data of flowing CNF

To demonstrate the application of the present reconstruction, the original SAXS distributions Ψ_{χ} from Håkansson et al.¹⁹ are used. The choice of N_{LP} must be done with care due to scatter in the experimental data. Figure 7a shows $\Psi_{\chi}^{(3D)}$ obtained at $z = 2.5h$ (h is the side of the quadratic cross-section of the flow-focusing device) from the SAXS experiments by Håkansson et al.¹⁹. Choosing $N_{LP} = 2$ (red dashed curve) to fit $\Psi_{\chi}^{(3D)}$ is not sufficient, but on the other hand choosing $N_{LP} = 15$ (blue thick solid curve) creates some "wiggles" in the fitted curve as the scatter in the data influences the fitting. This is even more apparent when

looking at the resulting distribution of Ψ_ϕ in figure 7b. When plotting the mean square error between the experimental data of $\Psi_\chi^{(3D)}$ and the fitted curve as function of N_{LP} in figure 7c it is clear that there really is no improvement of the fitting above $N_{LP} > 4$. We therefore implement a strategy to avoid overfitting by setting a stopping criteria based on the mean square error. The details are given in the supplementary information.

Using this strategy to find N_{LP} , the reconstruction method is applied to the original data by Håkansson et al.¹⁹. Figure 8a shows how the reconstructed S_ϕ differs from the value of S_χ . The value of S_ϕ is consistently higher than S_χ with a difference of around 0.05. Even though the alignment is mainly through uni-axial extension, the difference between S_ϕ and S_χ is much smaller than the prediction from the uni-axial extension curve in figure 5. This is most probably attributed to substantial rotary diffusion during the extension process. Consequently, the order parameter by Håkansson et al.¹⁹ is actually a decent estimate of S_ϕ .

Now, a comparison can be done with simulations using the Smoluchowski equation in eq. (6). As a boundary condition to the simulations, the ODF Ψ_ϕ at $z = -h$ is set to be the reconstructed ODF from Håkansson et al.¹⁹ at the same position. The centerline velocity $w_c(z)$ for the same flow conditions is taken from Håkansson et al.²⁰, which was obtained numerically through the two-fluid level set method with a core flow with kinematic viscosity of $\eta = 40$ mPa s and sheath flow of water. This centerline velocity was also verified experimentally through micro particle tracking velocimetry (μ PTV) by Håkansson et al.²⁰. Further parameters used in the present simulations are $\Lambda \approx 1$ and $D_r = 0.23$ rad²/s, where the latter is chosen to match the experimental data as well as possible.

The simulated results are illustrated with the blue line in figure 8a, where the order parameter S_ϕ is plotted versus the downstream position z . Although the model is not perfectly capturing the experiments, the qualitative appearance is fairly good and it could be potentially seen as a good model for the physical system. However, comparing the actual evolution of the ODFs at different downstream positions in figures 8b-c, it is found that the model does not perform very well in capturing the shape of the ODFs. The discrepancy

Figure 8: Results of the reconstructed order parameter S_ϕ from the SAXS measurements by Håkansson et al.¹⁹; the results are compared with the simulations using the Smoluchowski equation (eq. (6)); (a) order parameter as function of downstream position z ; the arrows indicate the positions that are used for the numerical drying experiments in figure 9; (b), (c) the evolution of the ODFs Ψ_ϕ at positions in the acceleration region of the channel and at positions after the focusing region; (d) shape parameter γ versus S_χ for the projected ODFs corresponding to the results in (a)-(c); the arrows show the evolution with increasing z ; the parameters γ and S_χ are compared with the ODFs corresponding to the results in figure 5 for $S_\chi \in [0.1, 0.8]$.

between simulation and experiment becomes even more evident in figure 8d, where the shape parameter γ is plotted versus S_χ . The figure also shows the corresponding shape parameters obtained for the simulated ODFs from figure 5 in the range $S_\chi \in [0.1, 0.8]$. Interestingly, the ODFs from the SAXS experiments show much more resemblance to the ODFs of Brownian rotary diffusion, while the ODFs from the simulations are closer to those obtained with pure extensional flow.

The poor correspondence between simulations and experiments is of course not very surprising, since the model chosen for this particular comparison in eq. (6) relies on many questionable assumptions; one of the more crucial being that the CNF dispersion is dilute and that fibrils do not interact. For future work, in order to improve the Smoluchowski model to account for concentration effects, additional modifications are needed, for example introducing a rotary diffusion coefficient that is dependent both on the concentration and the local ODF as done by Håkansson et al.²⁰.

3.4. Application to the drying process

In the process described by Håkansson et al.¹⁹, the aligned dispersion of CNF is locked in an arrested (gel) state when exiting the flow-focusing device. The gel thread is subsequently dried afterwards to form the final filament. During the removal of water from the gel, the cylindrical thread goes from a diameter of approximately 0.5 mm to 20 μm while maintaining the same length. The thread has thus shrunk radially with a ratio of $\beta = 20/500 = 0.04$. During the drying of the CNF gel, the radial component of the fibril orientation (in the cylindrical geometry given by the gel thread) is assumed to also decrease with the same shrinking ratio β . The result is that the z -component of the fibril orientation increases, and thus also the fibril alignment. This radial shrinking process will be used to simulate how the fibril alignment increases during the drying of the gel thread. The detailed mathematical description of the process is given in the supplementary information and a movie illustrating how fibrils align during this process is provided in the online supplementary material.

Figure 9: Results from the simulated drying process using initial ODFs Ψ_ϕ from four different positions: (a) $z = 2.5h$, (b) $4.5h$, (c) $9.5h$ and (d) $14.5h$ obtained by reconstructing the ODFs from the SAXS experiments by Håkansson et al.¹⁹; the results are compared with the actual WAXS data of the dried cellulose filament in Håkansson et al.¹⁹.

In the numerical drying simulations, it will be assumed that the gel-transition will lock the ODF in the dispersion at a certain downstream position z . Therefore, the reconstructed ODF Ψ_ϕ from the SAXS experiments at four different positions after the focusing section (pointed out with the small arrows in figure 8a) are used as initial ODF for the numerical drying simulations. These positions are $z = 2.5h$, $4.5h$, $9.5h$ and $14.5h$. The initial orientations ϕ_0 of the particles are randomly chosen from these ODF exactly as done previously. The initial angle θ_0 is again chosen from a uniform distribution. The system is then aligned by decreasing β from 1 to 0 to simulate the drying process.

The resulting ODFs after the numerical drying simulations are illustrated in figures 9a-d for different shrinking ratios β at the given downstream positions. As expected, assuming the drying process to be represented well by the radial shrinking principle, the alignment can increase substantially during the process. For example the initial distribution at $z = 14.5h$

goes from an order parameter of $S_\phi \approx 0.2$ to $S_\phi \approx 0.6$ during drying. As a matter of fact, even a completely random distribution ($S_\phi = 0$) is found to reach an alignment of $S_\phi = 0.5$ during this process (shown as a supplementary movie). As the shrinking process starts, the fibrils oriented in the $\phi = \pm\pi/2$ -plane are aligning quicker than the fibrils with lower $|\phi|$. The result is that there will be a sharp peak visible in the ODF. Assuming that there is some rotary diffusion present also during the drying process, either due to Brownian motion or fibril contacts, this peak will probably be smoothed out in reality.

To assess the validity of this principle, a comparison is made with the dried cellulose filament produced through the given flow conditions, which was presented by Håkansson et al.¹⁹. An ODF of the fibrils inside the filament was obtained through WAXS, which means that the presented ODF is a measurement of Ψ_χ . The alignment was found to be $S_\chi = 0.5$ and representing a projected mean fibril angle of $\langle\chi\rangle = \arccos \sqrt{(2S_\chi + 1)/3} = 35^\circ$. Assuming that the ODF of the azimuthal angle θ is uniform also in the filament, the ODF Ψ_ϕ is reconstructed in the same way as for the SAXS data. The order parameter with respect to the polar angle ϕ is found to be $S_\phi = 0.61$, with a corresponding mean fibril angle of $\langle\phi\rangle = \arccos \sqrt{(2S_\phi + 1)/3} = 31^\circ$. The alignment is thus actually higher than what was presented by Håkansson et al.¹⁹. However, even though the value of S_ϕ was substantially ($\approx 20\%$) higher, there was only a small decrease ($\approx 11\%$) of the mean fibril angle.

The data of the dried filament by Håkansson et al.¹⁹ is illustrated with the dashed curves in figures 9a-d. Observing first the simulated ODF from the position of maximum alignment ($z = 2.5h$) in figure 9a, it is seen that the ODF does not approach the distribution of the filament with decreasing β . Interestingly, the ODF of the dried cellulose filament obtained through WAXS seems to be very close to the numerical drying simulations at $z = 9.5h$ (figure 9c) and $z = 14.5h$ (figure 9d) for $\beta = 0.25$, assuming that the peak in the ODF is smoothed out. The close matching of the ODFs at least slightly strengthens the hypothesis that the drying process is mainly governed by the radial shrinking principle. The indication is also that the gelling in this case occurs somewhere around $z \approx 10h$. This is also in

good agreement with the results by Håkansson²⁸. The results also suggest that we could theoretically produce a filament with an order parameter of $S_\phi \approx 0.7$ and $\langle\phi\rangle = 27^\circ$, by just controlling the gelling at the present flow conditions to occur at the position of maximum alignment, i.e. at $z = 2.5h$. Of course, there are practical limitations to achieving this value as it also takes some time for the gel to form.

In conclusion, it is found here that a shrinking ratio of $\beta \approx 0.25$ seems to be enough to almost obtain the true ODF of the dried filament. In reality the expected shrinking ratio is however close to $\beta = 0.04$. The reason is believed to be that the true drying process probably is a lot more intricate than this naive model, especially in the final stages of the drying. As the particle concentration increases towards the end of the drying ($\beta < 0.25$), the particles might sterically hinder each other from aligning according to our simplified model.

4. Conclusions

In this work, we present a new way of reconstructing the three-dimensional ODF Ψ_ϕ by using measurements of the projected ODF Ψ_χ with SAXS. This method is applicable on any initial ODF and provides directly the order parameters of the system. The only assumption made is that the distribution of the azimuthal angle θ around the flow direction is uniform, i.e. the system has axial symmetry and Ψ_θ is constant; an assumption that is valid in a large range of flow systems or solid materials. The ODF Ψ_ϕ can then be used to compare with simulations of dispersed nanoparticles in order to understand more of the underlying physics. This method advances the knowledge to access the three-dimensional orientation using SAXS without having to rotate the sample, given that the assumption of axial symmetry is valid.

The reconstruction method was applied to revise the experimental results by Håkansson et al.¹⁹, who studied the hydrodynamic alignment and assembly of cellulose nanofibrils (CNF) in a flow-focusing device to produce continuous cellulose filaments. It is found in the present work that the three-dimensional alignment (represented by the order parameter S_ϕ)

is slightly higher than the previously presented projected alignment (represented by S_χ). A simple model to simulate the evolution of Ψ_ϕ in the flow-focusing device is applied by using the Smoluchowski equation, assuming no fibril interactions. Even though the evolution of S_ϕ versus downstream position could be qualitatively captured with this simple model, it is obvious that it does not simulate the true evolution of Ψ_ϕ as measured with SAXS.

Finally, the reconstruction was also applied to the ODF obtained through wide angle X-ray scattering (WAXS) experiments of a dried filament by Håkansson et al.¹⁹. It was found that the results were consistent with the assumption that the drying process is governed by a radial shrinking process as water is removed from the gel thread. However, the model developed here is too simple to explain quantitatively the full drying process. To further explore the dynamics during the drying process, additional in-situ SAXS/WAXS experiments can be conducted in the future, where the structure is studied during the actual drying similar to the study by Sen et al.²⁹.

The results in this work opens up new possibilities to study elongated nanoparticles in flows with axial symmetry and quantitatively compare experiments with numerical simulations. This will potentially lead to improved models and reveal the true mechanisms behind the angular dynamics of the dispersed nanoparticles. The future improved models should then be assessed by comparing the actual three-dimensional ODF in the channel rather than comparing only alignment.

Future research is also suggested in the direction of assessing the validity of a constant Ψ_θ . This can possibly be found by coupling the full three-dimensional version of the Smoluchowski equation to two-fluid simulations in the three-dimensional geometry. If Ψ_θ can not be assumed to be constant, the reconstruction method presented in this work will fail and it would require other considerations to obtain Ψ_ϕ from a measurement of Ψ_χ . However, recent advances in 3D tomographic SAXS^{16,17} could possibly be used also for flowing dispersions of nanoparticles. Using this technique, both Ψ_ϕ and Ψ_θ could possibly be obtained at a given position in space.

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Supplementary Material

1. Matlab code for reconstructing Ψ_ϕ from an input ODF Ψ_χ using $N_{LP} \in [1, 15]$.
2. Movie showing how isotropically distributed particles align during a radial shrinking process.

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Figure 10: TOC Graphic