Tumbling of Quantum Dots: Rheo-optics

Run Li,[†] Marisol Ripoll,^{*,‡} Naveen Reddy,^{*,‡,¶} Jan K.G. Dhont,^{§,||} Ruben

Dierick,[⊥] Zeger Hens,^{⊥,#} and Christian Clasen[@]

[†]*Theoretical Soft Matter and Biophysics, Institute of Complex Systems, Forschungszentrum
Jülich, 52425 Jülich, Germany*

[‡]*Hasselt University, Martelarenlaan 42, 3500 Hasselt, Belgium*

[¶]*IMO-IMOMEC, Wetenschapspark 1, 3590 Diepenbeek, Belgium*

[§]*Soft Matter , Institute of Complex Systems, Forschungszentrum Jülich, 52425 Jülich,
Germany*

^{||}*Heinrich-Heine Universität Düsseldorf, Department of Physics, 40225 Düsseldorf,
Germany*

[⊥]*Center for Nano- and Bio-photonics, Ghent University, 9052 Gent, Belgium*

[#]*Physics and Chemistry of Nanostructures, Ghent University, 9000 Gent, Belgium*

[@]*Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200 F, 3001 Leuven,
Belgium*

E-mail: m.ripoll@fz-juelich.de; naveen.reddy@uhasselt.be

Abstract

Linear flow dichroism is shown to be a powerful tool to characterize the hydrodynamic dimensions of extremely small non-spherical colloids in solution. Dispersions of prolate and oblate quantum dots (QD) are employed to investigate the validity of flow dichroism as a characterization tool. Shape-anisotropic QD are important from an application perspective, where it is necessary to have good knowledge of their hydrodynamic dimensions in order to predict and control their orientation during solution

processing. Flow dichroism quantifies the tumbling motion of QD in shear flow by optical means, which provides a characteristic signature of the particle shape, hydrodynamic friction, and size distribution. The effects of particle size and shape, size polydispersity, and shear rate on the temporal evolution of the flow-induced alignment is discussed in detail on the basis of numerical solutions of the Smoluchowski equation that describes the motion for the probability of the orientation of colloids in shear flow. It is shown that the combination of flow-dichroism experiments and the theoretical approach on the basis of the Smoluchowski equation provides a means to measure hydrodynamic aspect ratios and polydispersity, which for such small particles is not feasible with standard methods like light scattering. Flow dichroism will be useful not only for shape-anisotropic colloidal QD, but also for other nanoscale systems.

Introduction

Colloidal quantum dots (QD) are semiconductor nanocrystallites with sizes typically ranging between 2 and 20 nm.¹ Although such nanocrystals already have the crystal structure of their bulk counterparts, their opto-electronic properties are strongly size-dependent. Due to quantum confinement, the QD band gap increases with decreasing QD size, which results in a broadband absorption spectrum with a size-tunable absorption onset and a narrow photoluminescence spectrum with a central wavelength that concomitantly shifts to shorter wavelengths.² A further tuning of the opto-electronic properties is possible by exploiting shape anisotropy.^{3,4} Rod-like nanocrystals, for example, preferentially absorb and emit light linearly polarized along their long axis.^{5,6}

QD have gained attention as an optical material in lighting and display application,^{7,8} solar energy conversion,⁹ photodetection^{10,11} and lasing.^{12,13} In addition, they have raised extensive interest as a luminescent probe in biomedical applications, such as biolabeling and immunoassays.^{14–18} In almost all of these applications, QD are first dispersed in suitable liquid medium to form colloidal suspensions, and these QD dispersions are then processed

to obtain a desired QD-coating or QD-composite. For example, QD dispersed in a polymer solution can be spun into aligned nanowires to produce waveguides with high polarization ratio.¹⁹ Similarly, QD suspensions are used in other techniques such as electrohydrodynamic jet printing,²⁰ screen-printing,²¹ or roll-to-roll printing²² to control the deposition, distribution, and alignment. In all the above techniques, the rheological properties of the suspension play a crucial role not only to optimize processing conditions, but also to control the final alignment and ordering of nanoparticles.^{23,24}

The rheological properties of a particular colloidal suspension depend on a number of factors such as colloid concentration, shape of the colloids, and colloid-colloid interactions. While for very dilute solutions the colloid size has in principle no effect on the viscosity, for higher concentrated systems the effect of Brownian motion and its competition with the applied deformation rate strongly affects the flow properties and requires thus a detailed characterization of the colloid dimensions. Moreover, for nanocolloids the required stabilization in the form of colloid charge and an associated Debye length, or steric stabilization via grafted polymers or surfactants, will lead to an additional alteration of their effective hydrodynamic dimensions.^{25–30} Two geometric parameters that are particularly effective in influencing the rheological properties of a suspension during deposition are the shape anisotropy of the colloid, specifically the hydrodynamic aspect ratio, and the polydispersity thereof, which also plays a crucial role in the formation of more complex structures during post processing.^{23,24,31–33}

A problem that arises when characterizing these parameters is that although many techniques are available to obtain information on colloid dimensions and polydispersity, such as electron microscopy or UV-Vis spectrometry for gold and silver nanocolloids,^{34–36} they only provide absolute physical dimensions of the colloids and not rheologically relevant hydrodynamic dimensions. For anisotropic colloids, this effect is amplified when their size decreases to the nanometer regime, since the ratio of the thickness of the stabilizing layer and the dimension of the colloidal particles diverges when approaching the dimensions of QD. In

addition, these techniques provide statistically poor data due to the small sampling size. Other techniques, such as dynamic and depolarized dynamic light scattering that do provide statistically relevant hydrodynamic dimensions, are only suitable if the colloids are larger than the dimensions of the probe light.^{37,38} Furthermore, obtaining polydispersity using light scattering can be ambiguous due to the arising complex scattering patterns.³⁹ Given the typical sizes of QD (2-20 nm), investigations with scattering techniques therefore are usually not possible since each colloid acts as a Rayleigh point scatterer and hence does not provide any information about the colloidal shape.

One possibility to optically access the dimensions of QD is with linear flow dichroism (LFD). Dichroism measurements probe the polarization dependence of the turbidity that arises from scattering. The transmitted intensity is reduced due to scattering, while the scattered intensity depends on the polarization direction of the incident light for those cases where there is a preferred direction of orientation of shape-anisotropic colloids. Such a preferred direction of orientation can be induced when a colloidal suspension is subjected to a controlled flow field using for example a rheometer. Linear dichroism is then simultaneously probed using modulated polarized light.^{40,41} Colloids with an anisotropic shape tumble in such a flow field due to the differences in torque at either end of the colloid. For this, the hydrodynamic forces must be sufficiently large to overcome Brownian motion, and thus align the colloids on average towards the flow direction and rotate (tumble) them in the flow gradient plane. A sufficiently large Peclet number, $Pe = \dot{\gamma}/D_r$, to meet this requirement (where $\dot{\gamma}$ is the applied shear rate and D_r is the rotational diffusion coefficient of the colloid) can be achieved for nanocolloids by suspending the colloids in a high viscous, Newtonian matrix fluid. For the dimensions and rotational diffusivities of QD, viscosities on the order of 1-10 Pa s are sufficient to reduce Brownian rotational diffusion allowing to reach high Pe within an experimentally accessible shear rate-range of 1-10 s⁻¹.

Pioneering works from Fuller and co-workers⁴⁰⁻⁴⁴ on colloids of micron and sub-micrometer dimensions have shown that, using transient flow dichroism data, both the hydrodynamic

aspect ratio as well as polydispersity can be obtained simultaneously. Recently, LFD has been used by Vermant and coworkers to push the colloid diameter measurement limit down to 50 nm, using shape anisotropic gold nanocolloids. Although their minimum length scale was close to the Rayleigh scattering regime, they could still rely on the localized surface plasmon resonance of gold nanocolloids to resolve scattering along and across the length of nanocolloid to obtain dichroism and orientation angle.⁴⁵ Information about hydrodynamic aspect ratio and polydispersity for all the above cases was obtained by fitting the experimental LFD data to a simplified Smoluchowski equation with the assumptions of a very high Pe regime and near spherical colloids.

In this paper, we push the detection limit of LFD further down to particle dimensions of 10 nm to resolve the tumbling motion of QD, and extend the theoretical analysis to arbitrary values for Pe and arbitrary aspect ratios. We exploit the fact that QD retain their crystalline lattice structure even on their small dimensional scale. Measurements of the strong internal anisotropy of the lattice can be used as a 'pointer' for the colloid orientation, even for QD with a small shape anisotropy.

As dichroism is a measure of the change in the imaginary part of the refractive index, the oriented crystalline lattice of QD during tumbling leads to a significant change in dichroism even for the small dimensions of QD. Typically, dichroism values of around $1e-6$ to $1e-5$ represents a good signal-to-noise ratio.^{40,41} Recently, tumbling was captured with dichroism values reaching $1e-7$ for plasmonic gold rods and disks.⁴⁵ In this article we will show that with a low signal-to-noise ratio QD tumbling can be detected even at dichroism values of $1e-8$. Here, we show that linear flow dichroism can be used to determine the orientation and thus rotary motion of QD, from which both their hydrodynamic aspect ratio and polydispersity are obtained, quantities that have not yet been determined for QD by any other technique. As the QD are very small, reaching the very large Pe regime is experimentally not feasible. This implies that the existing approximations of tumbling theories valid in the high Pe regime⁴⁵ are not applicable. Therefore, we here present the use of the full Smoluchowski equation,

which is numerically solved to fit transient LFD data to obtain both hydrodynamic aspect ratio and polydispersity of QD at intermediate Peclet numbers where Brownian motion cannot be ignored.

Experimental Section

Synthesis of QD

CuInS₂ quantum dots (CIS QD) were synthesized through a method described before by Dierick et al.⁵¹ To obtain the relatively large, tile-shaped CIS nanocrystallites used here, 1 mmol of Cu(acac)₂ (0.262 g), 1 mmol of In(acac)₃ (0.412 g) and 2.1 mmol (0.067 g) elemental S were added to 30 mL of 1-octadecene in a three-neck flask. This flask was then attached to a Schlenk line, after which the heterogeneous mixture was flushed with nitrogen for 1 h. Next, 2 mL of oleylamine was injected, followed by increasing the temperature to 240 °C. An infrared heating lamp was used to fix the heating rate at 80 °C/min. Upon reaching 240 °C, the reaction was allowed to continue for 1 h. After this period, the flask was cooled down using a water bath, and the CIS QD were washed using toluene and ethanol. The nanocrystallites were then collected by centrifugation and the brown-red supernatant was discarded. The nanocrystallite pellet was redissolved in toluene and the resulting clear black solution was stored in the fridge. Under these synthesis conditions, we obtained tile shaped CIS QD (samples D and E in table 1).

CdSe/CdS nanorods (samples A, B and C in table 1) were synthesized according to an established procedure.⁵² First, CdSe cores (seeds) were synthesized in trioctylphosphineoxide (TOPO), using a mixture of cadmium oxide (CdO), octadecylphosphonic acid (ODPA), trioctylphosphine (TOP) and trioctylphosphineselenide (TOPSe) as precursors. In practice, 3.0 g of TOPO was mixed with 0.84 mmol (0.280 g) of ODPA and 0.47 mmol (0.060 g) of CdO. The mixture was degassed by exposing it to vacuum for 1 hour at 150 °C. Next, under inert atmosphere, the mixture was heated to 300 °C to dissolve all CdO and 1.5 g of TOP

was added as soon as a clear mixture was obtained. Afterwards, the temperature was further raised to 350 °C and 0.5 mL of a 1.7 M solution of Se in TOP was rapidly injected. The reaction was quenched after 1 min using a water bath and the thus obtained nanocrystals were separated from the reaction mixture by addition of methanol as a non-solvent and centrifugation. These CdSe nanocrystals were used as seeds to form CdSe/CdS nanorods. This involved a similar method starting from the same mixture of TOPO, ODPA and CdO in which a mixture of 2 mL TOP-S (2.4 M) and 50 nmol of CdSe was injected. The rod growth reaction was quenched after 8 min and the thus formed CdSe/CdS nanorods were separated from the reaction mixture by the addition of 5 mL toluene and 10 mL methanol when the reaction mixture had reached 80 °C. The nanorods were then immediately collected by centrifugation.

Linear flow dichroism measurements

Linear flow dichroism was measured using a home-built optical train combined with a Couette flow geometry in a stress controlled rheometer, MCR300 (Paar Physica, Austria).^{45,47} The optical train used to measure dichroism was designed following the rules laid out in Ref.⁴⁰ and is composed of a He-Ne laser ($\lambda = 632.8$ nm, 10 mW), a Glen-Thompson polarizer at 0° (Newport, USA), a photoelastic modulator at 45° (PEM, Beaglehole Instruments, New Zealand), a quarter-wave plate at 0° (Newport, USA), and a double prism to bend the horizontal light in the vertical direction such that it passes through the Couette cell along the shear-gradient plane, probing the tumbling of colloids. The scattered light emerging from the Couette cell after passing through the sheared sample is collected using a photodiode. The Couette cell was custom built with quartz disks at the top and bottom of the cell to provide optical access and to eliminate scattering from the air-liquid interface. The Couette cell has an inner radius of 16.95 mm, an outer radius of 17.95 mm, and a height of 21 mm. The photodiode provides two outputs, a direct current (DC), which provides the intensity of the scattered light, and the alternating current (AC), which contains the intensity fluctuations

due to the colloids tumbling. The AC signal is passed through a low-pass filter and sent to two lock-in-amplifiers (Stanford Research Systems Model 830) together with the signal from the PEM. The first (R_1) and the second (R_2) harmonic outputs from the lock-in-amplifiers, along with the DC signal, are used to obtain both the magnitude of dichroism and the orientation angle. The dichroism is given by⁴⁰

$$\Delta n'' = -\text{sgn}(R_2) \tanh^{-1} \left\{ \frac{1}{2} \sqrt{\frac{R_1}{-J_1(A)} + \frac{R_2}{-J_2(A)}} \right\} \times \frac{\lambda}{2\pi l} \quad , \quad (1)$$

where λ is the wavelength of light (632.8 nm), l is the optical path length (21 mm), J_1 and J_2 are Bessel functions of the zeroth order, and A is a constant that depends on the photoelastic-modulator, such that $J_0(A) = 0$. Similarly, the orientation angle, that is, the average angle of alignment of the colloids relative to the flow direction, is given by

$$\chi = \frac{1}{2} \tan^{-1} \left\{ \frac{R_1/J_1(A)}{R_2/J_2(A)} \right\} . \quad (2)$$

To reduce Brownian motion and to increase Pe within the experimentally accessible shear rates ($0.1\text{-}10 \text{ s}^{-1}$), the QD were dispersed in mineral oil with a viscosity of 4.9 Pa s. The setup was calibrated using the same mineral oil without QD. All experiments were conducted at 22 °C. Sample concentrations were adjusted to obtain an optical density around 0.5 at 632.8 nm.

Linear flow dichroism experiments were conducted on rod-like and disk-like quantum dots as those shown in fig 1, and whose physical dimensions, determined using TEM, are given in table 1. Note that these physical dimensions only represent core particle dimensions without taking into account other additional characteristics such as polymer coatings, or asymmetric charge distributions when dispersed in a liquid, or bullet shape for prolate QD and flat disk shape for oblate QD. These additional factors will be reflected in the hydrodynamic particle dimensions, which are crucial for determining the rheological properties of QD suspensions.

Table 1: Physical dimensions of the five analyzed samples of quantum dots obtained from TEM images. Here a refers to the radial length, b to the axial length, and $\bar{p}_{\text{TEM}}$ to the average aspect ratio. The lengths are given in nm.

Sample	description	a/b	$\bar{p}_{\text{TEM}}$
A	CdSe/CdS nanorod	17.3/4.6	3.76
B	CdSe/CdS nanorod	11.8/5.6	2.10
C	CdSe/CdS nanorod	12.1/3.8	3.18
D	CuInS ₂ tile	10.0/19.19	0.52
E	CuInS ₂ tile	7.77/15.38	0.50

Figure 1: Example of transmission electron images of rod-like (sample A) and disk-like (sample D) quantum dots.

Results and discussion

Linear flow dichroism (LFD)

LFD is one of the most effective techniques to determine the hydrodynamic aspect ratio and polydispersity of shape anisotropic colloids. Typically, a non-spherical colloidal particle in a shear flow performs tumbling or kayaking motions (Jeffrey orbits) if hydrodynamic forces are sufficiently large to overcome Brownian motion. The hydrodynamic forces result in a torque on the colloid that causes it to periodically tumble in the flow gradient plane. Such periodic orientational motions are referred to as Jeffrey orbits.⁴⁶ For negligible Brownian motion, the time period T for a tumbling event is given by,

$$T = \frac{2\pi}{\dot{\gamma}} \left\{ p + \frac{1}{p} \right\} \quad (3)$$

where p is the hydrodynamic aspect ratio of the colloid:⁴⁶ $p > 1$ for rod-like colloids, $p = 1$ for a sphere, and $p < 1$ for disk-like colloids. For an anisotropic colloid, the rotational velocity during a tumbling cycle is not constant since the colloid resides longer at orientations corresponding to lower hydrodynamic torques, which occurs when the long axis is parallel to the shearing direction. However, since the torque on any finite size colloid will not vanish completely, the colloid will eventually rotate out of this preferential position to quickly flip and approach this position again.

For long times and/or multiple colloids, an average tumbling period is determined from the overall orientational distribution function (ODF), which quantifies the probability for a colloid to attain a certain orientation at a certain time. At rest, Brownian force causes the colloid orientation to be uniformly distributed, so that each orientation is equally likely to occur. However, at the start-up of shear the colloid rotates quickly into the preferential flow aligned orientation and then performs its tumbling rotation. For samples with monodisperse colloids, and in the limit where Brownian motion can be neglected (limit of $Pe \rightarrow \infty$),

this synchronised tumbling motion will maintain its correlation indefinitely under an applied shear force. However, when Brownian motion is significant, and for samples with colloids that are polydisperse with respect to their aspect ratio, the tumbling motion, averaged over all colloids being present in the sample, loses its correlation in time, leading to phase mixing. At a fixed Pe , colloids with smaller hydrodynamic aspect ratios tumble faster than their larger counter parts, since the tumbling period is directly proportional to the hydrodynamic aspect ratio. As time progresses, the phase mixing dampens the optical response of the ODF (while maintaining the average tumbling period T) and eventually approaches an apparent steady state, corresponding to an average orientation angle of the colloid's long axis and the flow direction between 45° (isotropic) and 0° (perfect alignment along the flow direction) depending on Pe . Perfect alignment is only achieved when increasing the shear rate to infinitely large values, where Brownian motion can be neglected. It should be noted that, in the hydrodynamically dilute regime, the magnitude of the dichroism is a linear function of the concentration, whereas the orientation angle is independent of concentration. Because of this, the average orientation angle is the preferred quantity to analyse and to obtain the hydrodynamic aspect ratio and polydispersity.

Smoluchowski equation for tumbling of colloids

The Smoluchowski equation describes the time evolution of the probability distribution function $P(\hat{\mathbf{u}}, t)$ of the unit vector $\hat{\mathbf{u}}$ that characterizes the orientation of a colloid: $\hat{\mathbf{u}}$ is pointing along the long axis of the rod, or pointing along the normal to the face of a disk. For very dilute dispersions, where interactions between the colloids can be neglected, the Smoluchowski equation reads

$$\frac{\partial}{\partial t} P(\hat{\mathbf{u}}, t) = D_r \mathcal{R}^2 P(\hat{\mathbf{u}}, t) - \mathcal{R} \cdot \{ \omega P(\hat{\mathbf{u}}, t) \} , \quad (4)$$

where $\mathcal{R}(\cdots) = \hat{\mathbf{u}} \times \nabla_{\hat{\mathbf{u}}}(\cdots)$ is the rotation operator (with $\nabla_{\hat{\mathbf{u}}}$ the gradient operator with respect to the Cartesian coordinates of $\hat{\mathbf{u}}$). The above Smoluchowski equation (eq 4) does not include interactions between the colloidal particles, and therefore applies only to very dilute suspensions. The first term on the right hand-side accounts for orientational Brownian motion, and the second term describes the effect of shear flow, where ω is the resulting colloid angular velocity. This angular velocity corresponds to Jeffery orbits,⁴⁶ and can be written in vector form as

$$\omega = \dot{\gamma} \frac{p^2 - 1}{p^2 + 1} \hat{\mathbf{u}} \times (\mathbf{\Gamma} \cdot \hat{\mathbf{u}}) + \dot{\gamma} \frac{2}{p^2 + 1} \hat{\mathbf{u}} \times (\mathbf{\Omega} \cdot \hat{\mathbf{u}}). \quad (5)$$

For simple shear, with flow in the x-direction and the velocity gradient in the y-direction, the velocity gradient tensor $\mathbf{\Gamma}$ and the rotational part of the velocity-gradient tensor $\mathbf{\Omega}$ are, respectively:

$$\mathbf{\Gamma} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathbf{\Omega} = \frac{1}{2} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (6)$$

In the following, we explore the effect of aspect ratio, Peclet number, and polydispersity on the colloid orientation in a flow field using the full numerical solution of the Smoluchowski equation (eq 4). This will later allow us to fit actual experimental data to the corresponding numerical solution. Earlier related comparisons were performed by Mason *et al.*,⁴⁸ who performed experiments with millimeter sized rod-like colloids and obtained an almost exact fit to experimental data using a reduced Smoluchowski equation where Brownian motion was neglected. For colloids with dimensions in the millimeter to micrometer range, large Pe can be achieved with relative ease using standard rheometers with flow rates and matrix viscosities within the experimentally accessible range.^{41–44} The Mason approximation is valid in the infinite Peclet number limit, but for intermediate Pe , typical for smaller colloids, the

probability distribution function for the rod orientation can only be obtained by numerically solving the full Smoluchowski equation.

Dependence of the orientation angle on the strength of the applied flow

The tumbling of the orientation angle of a monodisperse sample of rods with small and a larger aspect ratio is displayed in fig 2 as a function of the strain. The Mason approximation (see supporting information for the detailed implementation) is plotted together with the numerical solution of the Smoluchowski equation (eq 4), for values of Pe ranging from $10^2 - 10^{10}$. Mason's approximation shows a perfect periodic tumbling motion where the orientation angle oscillates between $\pm\pi/4$ degrees with a period that is a function of the aspect ratio as given by the Jeffery expression in eq 3. The solutions of the Smoluchowski equation shown here correspond to finite values of Pe and thus show phase mixing, where the amplitude of the oscillating orientation angle χ decreases with increasing strain. This damping becomes stronger both with Pe and aspect ratio. The values of the Peclet number at which Mason's approximation (eq 4 without the first term) can be considered valid are surprisingly large, and these values increase with the aspect ratio. For rods with small aspect ratio (close to spheres) the tumbling in fig 2a shows reasonable agreement with Mason's approximation at $Pe = 10^4$, while for $p = 4$ in fig 2b agreement occurs only at $Pe = 10^{10}$, and for $p = 7$ in fig 2c Mason's approximation does not come close to the real values, even at enormously high shear rates.

The damped evolution of the orientation angle obtained from the numerical solution of the Smoluchowski equation at smaller values of the applied shear rate are shown for $p = 2$ in fig 3. For large enough values of Pe , the oscillations of the orientation angle eventually vanish at large strain values reaching a steady orientation angle of $\pi/4 > \chi_s > 0$. The amplitude and the number of oscillations before reaching the steady state also decrease with decreasing Pe , eventually disappearing. The strain at which the steady behaviour is reached

Figure 2: The orientation angle as a function of strain calculated from the Smoluchowski equation in eq 4 at large values of Pe and compared to Mason's approximation, for aspect ratios a) $p = 1.1$, b) $p = 4.0$, and c) $p = 7.0$.

also decreases with Pe , as well as the steady orientation values. In the case shown in fig 3, it can be seen that for $Pe = 50$ there is on average still one single oscillation observed, while lowering the flow rate to $Pe = 10$ the rotational diffusion dominates the flow and the rods reach the steady orientation angle even before the first tumbling event is completed.

Figure 3: Orientation angle as a function of strain for $p = 2$ showing damped oscillations in a large range of Pe values.

Figure 4 shows measurements of how the asymptotic orientation angle χ_s for very large strains, in the stationary state, varies as a function of Pe . Very small values of Pe (typically $Pe \lesssim 1$) show very small orientation approaching $\chi_s = \pi/4$, which corresponds to the isotropic state. At larger values of Pe , χ_s shows a clear power law decay with Pe . Solutions of the Smoluchowski equation are compared in fig 4 with hydrodynamic simulation results by Winkler *et al.*,⁴⁹ who used multiparticle collision dynamics coupled to molecular dynamics to determine the average asymptotic angles χ_s as a function of Pe for a bead model of rod like colloids with $p = 10$. The simulations showed an approximate power law behaviour $\chi_s \propto Pe^{-0.46}$ for $Pe > 5$, a behaviour also observed previously for flexible polymers in shear flow.⁵⁰ Our numerical results in fig 4 are in good agreement, showing a similar power law, for aspect ratios $p = 10$ and $p = 20$. Important to note is that the agreement of our results with the power law scaling does not require any additional fitting parameter. Numerical results

for a smaller aspect ratio of $p = 2$ in fig 4 show, however, a faster decrease of χ_s . This steeper slope reflects the fact that a rod of small aspect ratio is easier to orient towards the flow axis than large ones at the same Pe . Interestingly, from fig 4 it can be seen that for large enough aspect ratios, the asymptotic orientation angles do not depend on the colloid aspect ratio. We note that our theoretical prediction obtained numerically from the Smoluchowski equation (in eq 4) requires orders of magnitude less computing time than the simulation results.

Figure 4: Normalized asymptotic orientation angle (χ_s) as a function of Pe for $p = 2, 10$ and 20 , compared with the hydrodynamic simulation results for $p = 10$ from Ref.⁴⁹

Dependence of the orientation angle on the colloid aspect ratio

The aspect ratio of the rods has strong and non-trivial effects on the angular velocity and the time dependent orientation angle in shear flow. As can be seen in fig 5, the intrinsic shape of the curve changes when the aspect ratio is increased, given a constant value of Pe . On average, the colloids spend more time oriented in the flow direction when the aspect ratio is larger. At the same time, the oscillations show larger damping for larger aspect ratios. Comparing fig 5a and fig 5b, the amplitude and number of the oscillations at the

same aspect ratio is reduced as the Peclet number is decreased. Figure 4b clearly indicates that the aspect ratio (for $p > 3$) has only a small influence on the asymptotic angles χ_s for large Pe . This agrees with the conclusions previously derived from fig 4.

Figure 5: Orientation angle as a function of strain at various aspect ratios for a) $Pe = 10^4$ and b) $Pe = 10^2$.

The period of the tumbling rotations can be characterized via the first half period $\tilde{T}_{12}$, which can be obtained from the strain at which the first minimum of the average orientation angle is found, as seen for example in fig. 5. The strains at these first half-periods are displayed in fig 6 as a function of the aspect ratio and the Peclet number, and are compared

with the prediction provided by Jeffery’s theory in eq 3.⁴⁶ Figure 6a shows how the full Jeffery approximation gradually deviates from the solution of the full Smoluchowski equation with increasing aspect ratio and decreasing Pe . Furthermore, Fig.6a shows that the rotation period at large applied shears grows approximately with $(p + 1/p)$ as predicted by Jeffery, while it becomes almost independent of the aspect ratio for the smallest applied shears. In order to analyze the dependence of the actual rotation period on the Peclet number, it is illustrative to display the half-period strains normalized by the corresponding Peclet number (this is also the period) times the rotational diffusion factor (which is constant for each value of the aspect ratio), as shown in Fig. 6b. The Jeffery approach considers no thermal motion at all, such that rotational diffusion can be considered to be vanishing. This means that a direct comparison is not really possible, although the dependence on the applied shear and aspect ratio can still be contrasted. The decay with the Peclet number rotation period appears to be a power law in Fig. 6b, but with an exponent smaller than one in the presence of thermal noise, a decay which appears to be slower the larger the aspect ratio is.

Dependence of the orientation angle on sample polydispersity

In addition to the effects of shear rate and aspect ratio on the temporal behaviour of the orientation angle, also the sample polydispersity can have a large influence. Although we consider the effect on dilute samples, where no interactions are taken into account, measurements are performed which probe an average over a large number of colloids. Realistic dispersions are sometimes quite polydisperse, containing a wide variety of, for example, rods with different lengths. To analyze the effect of polydispersity, the Smoluchowski equation 4 is solved for a number of different aspect ratios, and the resulting orientation angles are then averaged according to a log-normal distribution of the aspect ratio. The parameter σ that quantifies the degree of polydispersity is the width of the log-normal distribution (see the supplementary information for more details). The effect of polydispersity is shown in fig 7 as a function of strain for a fixed $p = 2$ and for two Peclet numbers $Pe = 10^4$ and 10^2 .

Figure 6: a) Strain at the first half-period as a function of the aspect ratio p for several values of Pe . Solid line correspond to the prediction by the Jeffery orbits in eq 3, and the dashed lines are guides to the eye. b) Rotation half period adimensionalized with the rotational diffusion as a function of the Peclet number for two values of the aspect ratio. Solid line indicates the inverse linear dependence predicted by Jeffery, and dashed lines indicate power law decays with exponents smaller than one.

Increasing polydispersity σ lead to the expected increased damping of the oscillations, and the effect is stronger for larger Pe , as can be seen by comparing fig 7a and fig 7b. Since the period of revolution of a colloid depends on its aspect ratio, each colloid length will tumble with a different frequency, which clearly results in phase mixing.

Figure 7: Orientation angle as a function of strain for varying polydispersity and $p = 2$ at a) $Pe = 10^4$ and b) $Pe = 10^2$.

Numerical fit to experimental dichroism data

The previously discussed features of the temporal evolution of the orientation angle (effect of shear rate, aspect ratio, and polydispersity) allow us to fit our numerical results to experimental data. The three related parameters Peclet number (Pe), polydispersity (σ), and aspect ratio (p), which are in principle unknown for the our QD suspensions, can therefore be determined. For the expected aspect ratio range of the QD measured in this study, and the experimentally accessible Pe , the tumbling period T will exhibit only a weak dependence on the Peclet number as can be concluded from our numerical results shown in fig 2, fig 3, and fig 6, as well as on the polydispersity σ as shown in fig 7. We therefore initially fit the four measured shear rate data to the same tumbling period T to obtain a unique estimated Pe and p (see fig 8) for the sample A. Subsequently, the following fitting procedure is used to obtain the hydrodynamic aspect ratio and polydispersity:

1. Experimental determination (for example via microscopy) whether the colloids are prolate (rod-like with $p > 1$), or oblate (disk-like with $p < 1$).
2. First estimation of the colloid aspect ratio (p) from the first half-period ($\tilde{T}_{12}$) of the time dependent average orientation angle.
3. Estimation of the value of Pe from the asymptotic orientation angle χ_s .
4. Solution of the Smoluchowski equation using the previously obtained p and Pe and assuming $\sigma = 0$, and subsequent optimization of the agreement of $\tilde{T}_{12}$ and χ_s by iteratively modifying the values of Pe and p .
5. Improving the matching of the oscillation amplitudes by solving the Smoluchowski equation with higher values of the polydispersity σ .

A comparison of fitting result to experimental data for sample A is shown in fig 8, where a good agreement of the tumbling period, the asymptotic behaviour at larger strains, and the decay in oscillation amplitude can be observed. Fitting curves obtained using the same method for other samples are shown in fig 9 where the method is applied for both, rod-like QD (samples B, C) and disk-like QD (samples D, E). The fitted values of p , σ , and Pe for

Figure 8: Comparison of experimental orientation angle as a function of strain for sample A to the prediction given by Smoluchowski equation (eq 4) with $p = 2.1$, $\sigma = 0.08$ and $Pe = 100$.

both rod and disk shape quantum dots are listed in table 2.

The hydrodynamic aspect ratio obtained from LFD is consistently smaller than the aspect ratio obtained from TEM, as shown in table 2. This is expected, as our QD colloids are coated with a stabilizing polymer layer that decreases the effective $\bar{p}$, and which is detected by LFD but not with TEM and explains the difference between the $\bar{p}$ from LFD and $\bar{p}_{\text{TEM}}$ data for the prolate particles in table 2. For the oblate QD a uniform polymer layer alone can not explain the difference between the LFD and TEM results. A similar finding for oblate particles has been reported before.⁴⁵ A plausible explanation for the discrepancy in case of the oblate QD is that the stabilization polymer layer is not homogeneously distributed over their surface. It seems that the polymer coating at the edges of the oblate QD is slightly denser as compared to the flat face, although there is no independent proof that sustains this observation. However, this supports the necessity of independent direct measurements of the hydrodynamic aspect ratio as with the LFD presented here, as not even the knowledge of the protective layer allows to fully theoretically predict the effective $\bar{p}$. But it should also be

Figure 9: Orientation angle as a function of strain comparing experiments and the Smoluchowski equation for samples B-E.

noted that the experimental LFD data have a rather large scatter, which is connected to the extremely small size of the QDs, leading to a small signal to noise ratio. This large scatter in the experimental data does not permit to make independent fits for each applied shear rate separately, but only to provide an average fit which corresponds to an average shear rate. In spite of this, a combination of experimental LFD and the fitting procedure using the Smoluchowski equation at intermediate Pe gives a robust estimate of the hydrodynamic aspect ratio and polydispersity for shape anisotropic QDs.

Table 2: Estimated average hydrodynamic aspect ratio, polydispersity, and Peclet number. The last column shows the physical aspect ratio from TEM for comparison.

Sample	$\bar{p}$	σ	Pe	$\bar{p}_{\text{TEM}}$
A	2.10 ± 0.10	0.08 ± 0.05	100	3.76
B	1.80 ± 0.10	0.07 ± 0.04	70	2.10
C	2.00 ± 0.14	0.07 ± 0.05	90	3.18
D	0.45 ± 0.02	0.07 ± 0.02	100	0.52
E	0.40 ± 0.03	0.06 ± 0.02	160	0.50

It should also be noted that our theoretical approach in eqs. (4) and (5) treats the particles as perfectly axisymmetric by describing their anisotropy with a single parameter, the aspect ratio p . Nevertheless, fig. 1 clearly shows discrepancies from this assumption, being easily identifiable as for example bullet shaped particles in fig. 1a, or hexagonal particles in fig. 1b. A study of the motion under shear of non-perfectly axisymmetric particles has shown⁵³ relatively large changes of the particle's rotation with respect to perfectly axisymmetric particles. However, the changes are large though only over periods of time that are long compared to a single tumbling period. This is because they are originating from the accumulation of small instantaneous alternations of the particle motion. These changes have been further proved to lead to measurable modifications of the suspension rheology.^{54,55} Therefore, we do not expect the deviations from the axisymmetric shape to have a significant effect in our LFD measurements, since the relevant time scales are comparable to the single particle tumbling period scale, at which the accumulative modifications on particle rotation are still negligible. On the other hand, extending the present theoretical approach to allow

for the investigation of non-axisymmetric particles is not straightforward, since it would require the generalization of the functional dependence of the angular velocity in Eq. 5, which is not trivial even for the case of triaxial particles.

Conclusions

Combining experimental rheo-optics and the numerical solution of the Smoluchowski equation is a powerful approach to characterize the effective aspect ratio of anisotropic colloidal systems for which other techniques fail, as is the case with quantum dots (QD) dispersed in a liquid. For this the time evolution of the orientation angle of dilute suspensions of non-spherical colloids upon inception of shear flow is monitored by means of a polarisation modulation method that probes linear flow dichroism (LFD). The time evolution of the orientation angle depends on three parameters: the Peclet number Pe , the hydrodynamic aspect ratio p , and the particle polydispersity σ . Numerical solutions of the rotational Smoluchowski equation for prolate and oblate colloids, including both Brownian motion and shear flow, reveal the importance of these parameters on the temporal evolution of the degree of alignment as quantified by the orientation angle. Based on this an analysis procedure for experimental LFD data is proposed for arbitrary values of Pe , p , and σ . Interestingly, although the LFD signal-to-noise ratio is low due to the small size of the QD, the hydrodynamic aspect ratio and polydispersity of QD can still be obtained reliably, which has been shown here for both prolate and oblate QD. We expect that this optical technique probing dichroism, and the data analysis based on numerical solutions of the orientational Smoluchowski equation, will be widely used for the characterization of the hydrodynamic properties of single particles ranging in sizes down to those of QD. We also anticipate that by matching the refractive index of the suspending medium to that of the particles, the method will soon be extended to the characterization of dense systems, where particle-particle interactions becomes important. Eqs. (3, 4 and 5) assume prolate- or oblate-shaped colloids. It is in principle possible

to extend our method to more complex-structured colloids. This is, however, not straightforward. First of all, the Smoluchowski equation should be extended to include bi- or even tri-axiality where two or three mutually coupled orientations are involved, and secondly the relation between the tumbling frequency and shape parameters must be determined from hydrodynamic numerical calculations and/or simulations. Once this is accomplished, the experimental method can be applied in the same way as for oblate and prolate colloids.

Acknowledgement

This project has received funding from the European Union within the Horizon 2020 project under the DiStruc Marie Skłodowska Curie innovative training network; Grant Agreement No. 641839. NKR and CC would like to acknowledge support from the Research Foundation Flanders (FWO), grant no. G077916N. RD, CC and ZH acknowledge financial support via the SBO-project QDOCCO within the SIM SoPPoM+ program of the Flemish Strategic Initiative for Materials (SIM).

References

- (1) Kovalenko, M. V. et al. Prospects of Nanoscience with Nanocrystals. *ACS Nano* **2015**, *9*, 1012–1057.
- (2) Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* **1996**, *271*, 933–937.
- (3) Krahne, R.; Morello, G.; Figuerola, A.; George, C.; Deka, S.; Manna, L. Physical properties of elongated inorganic nanoparticles. *Phys. Rep.* **2011**, *501*, 75–221.
- (4) Cunningham, P. D.; Souza, J. B.; Fedin, I.; She, C. X.; Lee, B.; Talapin, D. V. Assessment of Anisotropic Semiconductor Nanorod and Nanoplatelet Heterostructures

- with Polarized Emission for Liquid Crystal Display Technology. *ACS Nano* **2016**, *10*, 5769–5781.
- (5) Sitt, A.; Salant, A.; Menagen, G.; Banin, U. Highly Emissive Nano Rod-in-Rod Heterostructures with Strong Linear Polarization. *Nano Letters* **2011**, *11*, 2054–2060.
 - (6) Kamal, J. S.; Gomes, R.; Hens, Z.; Karvar, M.; Neyts, K.; Compennolle, S.; Vanhaecke, F. Direct determination of absorption anisotropy in colloidal quantum rods. *Phys. Rev. B* **2012**, *85*, 035126.
 - (7) Shirasaki, Y.; Supran, G. J.; Bawendi, M. G.; Bulovic, V. Emergence of colloidal quantum-dot light-emitting technologies. *Nat. Photonics* **2013**, *7*, 13–23.
 - (8) Shimizu, K. T.; Böhmer, M.; Estrada, D.; Gangwal, S.; Grabowski, S.; Bechtel, H.; Kang, E.; Vampola, K. J.; Chamberlin, D.; Shchekin, O. B.; Bhardwaj, J. Toward commercial realization of quantum dot based white light-emitting diodes for general illumination. *Photonics Res.* **2017**, *5*, A1–A6.
 - (9) Carey, G. H.; Abdelhady, A. L.; Ning, Z. J.; Thon, S. M.; Bakr, O. M.; Sargent, E. H. Colloidal Quantum Dot Solar Cells. *Chem. Rev.* **2015**, *115*, 12732–12763.
 - (10) Rauch, T.; Boberl, M.; Tedde, S. F.; Furst, J.; Kovalenko, M. V.; Hesser, G. N.; Lemmer, U.; Heiss, W.; Hayden, O. Near-infrared imaging with quantum-dot-sensitized organic photodiodes. *Nat. Photonics* **2009**, *3*, 332–336.
 - (11) Malinowski, P. E.; Georgitzikis, E.; Maes, J.; Vamvaka, I.; Frazzica, F.; Van Olmen, J.; De Moor, P.; Heremans, P.; Hens, Z.; Cheyns, D. Thin-Film Quantum Dot Photodiode for Monolithic Infrared Image Sensors. *Sensors* **2017**, *17*, 2867.
 - (12) Fan, F. J. et al. Continuous-wave lasing in colloidal quantum dot solids enabled by facet-selective epitaxy. *Nature* **2017**, *544*, 75–79.

- (13) Xie, W.; Stöferle, T.; Rainò, G.; Aubert, T.; Bisschop, S.; Zhu, Y.; Mahrt, R. F.; Geiregat, P.; Brainis, E.; Hens, Z.; Van Thourhout, D. On-Chip Integrated Quantum-Dot/Silicon-Nitride Microdisk Lasers. *Adv. Mater.* **2017**, *29*, 1604866.
- (14) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. Quantum Dots for Live Cells, in Vivo Imaging, and Diagnostics. *Science* **2005**, *307*, 538–544.
- (15) Beloglazova, N. V.; Goryacheva, I. Y.; Niessner, R.; Knopp, D. A. Comparison of Horseradish Peroxidase, Gold Nanoparticles and Quantum Dots as Labels in Non-instrumental Gel-Based Immuno-assay. *Microchim. Acta.* **2011**, *175*, 361–367.
- (16) Dabbousi, B.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. (CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. *J. Phys. Chem. B* **1997**, *101*, 9463–9475.
- (17) Liu, W.; Howarth, M.; Greytak, A. B.; Zheng, Y.; Nocera, D. G.; Ting, A. Y.; Bawendi, M. G. Compact Biocompatible Quantum Dots Functionalized for Cellular Imaging. *J. Am. Chem. Soc.* **2008**, *130*, 1274–1284.
- (18) Vinayaka, A. C.; Basheer, S.; Thakur, M. S. Bioconjugation of CdTe Quantum Dot for the Detection of 2,4-Dichlorophenoxyacetic Acid by Competitive Fluoroimmunoassay Based Biosensor. *Biosens. Bioelectron* **2009**, *24*, 1615–1620.
- (19) Aubert, T.; Palangetic, L.; Mohammadimasoudi, M.; Neyts, K.; Beeckman, J.; Clasen, C.; Hens, Z. Large-Scale and Electroswitchable Polarized Emission from Semiconductor Nanorods Aligned in Polymeric Nanofibers. *ACS Photonics* **2015**, *2*, 583–588.
- (20) Bong Hoon, K. et al. High-resolution patterns of quantum dots formed by electrohydrodynamic jet printing for light-emitting diodes. *Nano letters* **2015**, *15*, 969–973.

- (21) Kokkinos, C.; Prodromidis, M.; Economou, A.; Petrou, P.; Kakabakos, S. Quantum dot-based electrochemical DNA biosensor using a screen-printed graphite surface with embedded bismuth precursor. *Electrochem. Commun.* **2015**, *60*, 47–51.
- (22) Wang, X. Recent progress in colloidal quantum dot photovoltaics. *Front. Optoelectron.* **2015**, *8*, 241–251.
- (23) Dugyala, V. R.; Daware, S. V.; Basavaraj, M. G. Shape anisotropic colloids: synthesis, packing behavior, evaporation driven assembly, and their application in emulsion stabilization. *Soft Matter* **2013**, *9*, 6711–6725.
- (24) Glotzer, S. C.; Solomon, M. J. Anisotropy of building blocks and their assembly into complex structures. *Nat. Mater.* **2007**, *6*, 557–562.
- (25) Mewis, J.; Wagner, N. J. *Colloidal Suspension Rheology*; Cambridge University Press, 2012.
- (26) Lettinga, M. P.; Dhont, J. K. G.; Zhang, Z.; Messlinger, S.; Gompper, G. Hydrodynamic interactions in rod suspensions with orientational ordering. *Soft Matter* **2010**, *6*, 4556–4562.
- (27) Dhont, J. K. G.; Kang, K. Electric-field-induced polarization and interactions of uncharged colloids in salt solutions. *Eur. Phys. J. E* **2010**, *33*, 51–68.
- (28) Kang, K.; Wilk, A.; Patkowski, A.; Dhont, J. K. G. Diffusion of spheres in isotropic and nematic networks of rods: Electrostatic interactions and hydrodynamic screening. *J. Chem. Phys.* **2006**, *126*, 214501.
- (29) Kang, K.; Dhont, J. K. G. Double-layer polarization induced transitions in suspensions of colloidal rods. *Europhys. Lett.* **2008**, *84*, 14005.
- (30) Kang, K.; Dhont, J. K. G. Electric-field induced transitions in suspensions of charged colloidal rods. *Soft Matter* **2010**, *6*, 273–286.

- (31) Dugyala, V. R.; Basavaraj, M. G. Control over Coffee-Ring Formation in Evaporating Liquid Drops Containing Ellipsoids. *Langmuir* **2014**, *30*, 8680–8686.
- (32) Lama, H.; Mondal, R.; Basavaraj, M. G.; Satapathy, D. K. Cracks in dried deposits of hematite ellipsoids: Interplay between magnetic and hydrodynamic torques. *J. Colloid Interface Sci.* **2018**, *510*, 172–180.
- (33) Hamon, C.; Novikov, S.; Scarabelli, L.; Basabe-Desmonts, L.; Liz-Marzan, L. M. Hierarchical Self-Assembly of Gold Nanoparticles into Patterned Plasmonic Nanostructures. *ACS Nano* **2014**, *8*, 10694–10703.
- (34) Winckelmans, N.; Altantzis, T.; Grzelczak, M.; Sanchez-Iglesias, A.; Liz-Marzan, L. M.; Bals, S. Multimode Electron Tomography as a Tool to Characterize the Internal Structure and Morphology of Gold Nanoparticles. *J. Phys. Chem. C* **2018**, *in press*.
- (35) Bals, S.; Goris, B.; Liz-Marzan, L. M.; G., V. T. Three-Dimensional Characterization of Metal Nanoparticles and their Assemblies by Electron Tomography. *Angew. Chem. Int. Ed.* **2014**, *53*, 10600–10610.
- (36) Grzelczak, M.; Sanchez-Iglesias, A.; Liz-Marzan, L. M. A General Approach toward Polymer-Coated Plasmonic Nanostructures. *Cryst. Eng. Comm* **2014**, *16*, 9425–9429.
- (37) Berne, B. J.; Pecora, R. *Dynamic light scattering: with applications to chemistry, biology, and physics*; Dover Publications, 2000.
- (38) van de Hulst, H. C. *Light scattering by small particles*; New York (John Wiley and Sons), 1957.
- (39) Dhont, J. K. G. *An Introduction to Dynamics of Colloids*; Elsevier: Amsterdam, The Netherlands, 1996.
- (40) Fuller, G. G. *Optical rheometry of complex fluids*; Oxford University Press: Oxford, 1995.

- (41) Vermant, J.; Yang, H.; Fuller, G. G. Rheooptical determination of aspect ratio and polydispersity of nonspherical particles. *AIChE J.* **2001**, *47*, 790.
- (42) Frattini, P. L.; Fuller, G. G. The dynamics of dilute colloidal suspensions subject to time-dependent flow-fields by conservative dichroism. *J. Colloid Interface Sci.* **1984**, *2*, 506.
- (43) Frattini, P. L.; Fuller, G. G. Conservative dichroism of a sheared suspension in the Rayleigh-Gans light-scattering approximation. *J. Colloid Interface Sci.* **1987**, *119*, 335.
- (44) J., J. S.; G., F. G. The optical anisotropy of sheared hematite suspensions. *J. Colloid Interface Sci.* **1988**, *124*, 441.
- (45) Reddy, N. K.; Perez-Juste, J.; Pastoriza-Santos, I.; Lang, P. R.; Dhont, J. K. G.; Liz-Marzan, L. M.; Vermant, J. Flow Dichroism as a Reliable Method to Measure the Hydrodynamic Aspect Ratio of Gold Nanoparticles. *ACS Nano* **2011**, *5*, 4935–4944.
- (46) Jeffery, G. B. , The motion of ellipsoidal particles immersed in a viscous fluid. *Proc. Roy Soc. Ser. A* **1922**, *102*, 161.
- (47) Pellens, L.; Vermant, J.; Mewis, J. Deviations from the stress-optical relation in telechelic associative polymer solutions. *Macromolecules* **2005**, *38*, 1911.
- (48) Okagawa, A.; Cox, R. G.; Mason, S. G. The Kinetics of Flowing Dispersions. VI Transient Orientation and Rheological Phenomena of Rods and Discs in Shear Flow. *J. Coll. Interf. Sci.* **1973**, *45*, 3003–329.
- (49) Winkler, R. G.; Mussawisade, K.; Ripoll, M.; Gompper, G. Rod-like colloids and polymers in shear flow: a multi-particle-collision dynamics study. *J. Phys.: Condens. Matter* **2004**, *16*, 3941.
- (50) Aust, C.; Köger, M.; Hess, S. Structure and dynamics of dilute polymer solutions

- under shear flow via nonequilibrium molecular dynamics. *Macromolecules* **1999**, *32*, 5660–5672.
- (51) Dierick, R.; Van den Broeck, F.; De Nolf, K.; Zhao, Q.; Vantomme, A.; Martins, J. C.; Hens, Z. Surface Chemistry of CuInS₂ Colloidal Nanocrystals, Tight Binding of L-Type Ligands. *Chem. Mater.* **2014**, *26*, 5950–5957.
- (52) Carbone, L. et al. Synthesis and Micrometer-scale Assembly of Colloidal CdSe/CdS Nanorods Prepared by a Seeded Growth Approach. *Nano Lett.* **2007**, *7*, 2942–2950.
- (53) Hinch, E. J.; Leal, L. G. Rotation of small non-axisymmetric particles in a simple shear flow. *J. Fluid Mech.* **1979**, *3*, 591–607.
- (54) Rallison, J. M. The effects of Brownian rotations in a dilute suspension of rigid particles of arbitrary shape. *J. Fluid Mech.* **1978**, *2*, 237–263.
- (55) Almondo, G.; Einarsson, J.; Angilella, J. R.; Mehlig, B. Intrinsic viscosity of a suspension of weakly Brownian ellipsoids in shear. *Phys. Rev. Fluids* **2018**, *3*, 064307.

Graphical TOC Entry