Orientation dependent Stokes drag in a colloidal liquid crystal

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Stokes drag on the (sub)micrometre scale plays a key role in phenomena ranging from Brownian motion to the rheology of particulate suspensions. We report the first measurement of the direction dependent Stokes drag in a nematic liquid crystal of colloidal rods, where the viscous forces are of equal importance to the elastic forces. By tracking a sedimenting sphere with combined fluorescence confocal microscopy and polarization microscopy we find that the Stokes drag for motion along the director is two times larger than for motion perpendicular to the director. This brings the unique viscoelastic properties of a colloidal liquid crystal into focus.

The Stokes drag force $F_s = 6\pi\eta av$, experienced by a sphere with radius a moving at velocity v in a viscous medium with viscosity η, plays an important role in phenomena such as Brownian motion[1] and hydrodynamic interactions between moving particles.[2] In anisotropic media like liquid crystals, theory predicts a Stokes drag which depends on the direction of motion relative to the director.[3,4] This has been confirmed experimentally for thermotropic nematic liquid crystals, from diffusion coefficients of tracer droplets determined by video microscopy[5] and optical trapping of tracer spheres.[6] Here we report the first measurement of the orientation dependent Stokes drag in a colloidal nematic liquid crystal. We achieve this by studying a sedimenting fluorescent glass bead with simultaneous fluorescence confocal microscopy and polarization microscopy. This application of the falling sphere method[7] on the micrometre scale enables the measurement of local Stokes drag as a function of director orientation.

Laser scanning confocal microscopy, with its high contrast and the elimination of out-of-focus light by the use of a pinhole, enables accurate tracking of the tracer sphere position.[8] At the same time the orientation of the local director field is visualized by polarization microscopy, combined with the laser scanning confocal microscope in a single setup [see Fig 1(a)]. A Nikon C1 confocal scanhead was mounted on a Nikon Eclipse E400 polarization microscope, with the focal plane along gravity. Two light sources were used: the white light of the polarization microscope and the 488 nm laser of the confocal unit. The light coming out of the sample is transported through an optical fibre to the three confocal detector channels. The complete detector unit consists of two dichroic mirrors and three sets of high and low band pass filters, which guide the light to one of three photo multiplier tubes. The green light confocal detector channel (wavelengths 515–530 nm) was used for tracking of the fluorescent tracer sphere. The blue (wavelengths 435–450 nm) and red (wavelengths 605–675 nm) light confocal detector channels were used to determine the director orientation of the nematic phase from the optical path difference (OPD) of the transmitted polarized light. The OPD of a birefringent nematic phase is given by Δnd with Δn the birefringence of the nematic phase and d the sample path length. By using a retardation plate (λ-plate, within this experiment λ = 530 nm) an additional OPD is introduced. The resultant OPD and the corresponding interference colours depend on the orientation of the nematic director with respect to the retardation plate. When the director is parallel to the slow axis of the retardation plate, the OPD of the nematic phase is added to the OPD of the retardation plate, while in the perpendicular orientation it is subtracted.[9] To enable the measurement of the OPD with the confocal detector, the red over blue intensity ratio was measured as a function of the OPD (which was varied with a Babinet compensator[10]), as shown in Fig 1(b). The red over blue intensity ratio is appropriate for measuring the OPD because it is independent of the absolute light intensity and it has a straightforward correlation with the OPD in the range present in the samples to be studied.

We used this technique to study the orientation dependent Stokes drag in an isotropic–nematic phase separated system of colloidal boehmite rods [see Fig 2], charge stabilized with aluminum chlorohydrate.[11] This system is eminently suited to demonstrate the method. First of all the OPD for a convenient sample thickness (300 μm) with retardation plate is in a range (530 ± 50 nm) where it can be probed unambiguously with the red over blue transmitted light intensity ratio, as indicated by the dashed lines in Fig 1(b). This has the additional advantage that the interference colours can be probed by only using the blue and red light channels of the confocal detector. This is illustrated in Fig 3 where the interference colours obtained with the blue and red light channels of the confocal detector are compared with the interference colours obtained with a digital camera. From these pictures it also appears that the nematic phase consists of multiple domains with different director orientations, which allows for probing sedimentation velocities in different director orientations in a single experiment. Furthermore, the gravitational length of the rods ($L_g = \frac{k_B T}{m^* g}$ with k_B the Boltzmann constant, T the temperature, m^* the buoyant mass of the rods = 1.8×10^{-20} kg, and g the gravitational constant) is 2.4 cm, such that density gradients over the size of the sample are modest. Silica beads of 10 μm in diameter were coated with fluorescein and also charge stabilized with aluminum chlorohydrate, to serve as tracer spheres. Fig 4(a) presents a typical image of such a tracer sphere sedimenting towards the isotropic–nematic interface, as visualized with all three channels of the confocal detector.

The height profile in Fig 4(b) reveals that the sedimentation velocity of the sphere decreases upon entering the nematic phase in a domain with the director is parallel to gravity. The sphere subsequently enters a domain with the director perpendicular to gravity, where the sedimentation velocity increases again. The effective

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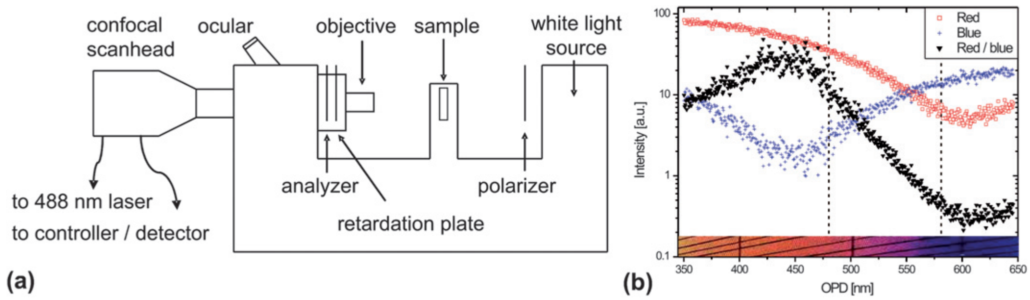

Fig. 1 (a) Schematic drawing of laser scanning confocal microscopy and polarization microscopy in a single setup. For conventional polarization microscopy the confocal scanhead is replaced by a digital camera. (b) Measurement of the red (red points) and blue (blue points) detector intensities and their ratio (black points) as a function of OPD varied with a Babinet compensator. The interference colours corresponding to the OPD are shown at the bottom of the graph.[9] The dashed lines indicate the OPD range present in the samples, with the lowest OPD corresponding to the nematic director oriented perpendicular, and the highest OPD corresponding to the nematic director oriented parallel to the slow axis of the retardation plate.

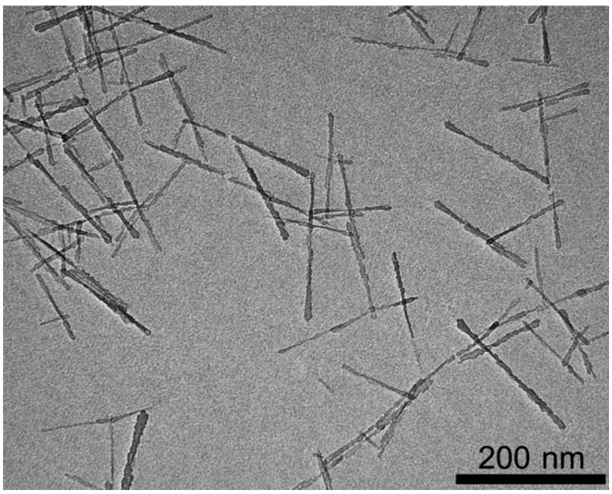

Fig. 2 Transmission electron micrograph of the colloidal boehmite rods, with a length of 150 nm and a thickness of 8 nm (both ± 40%).

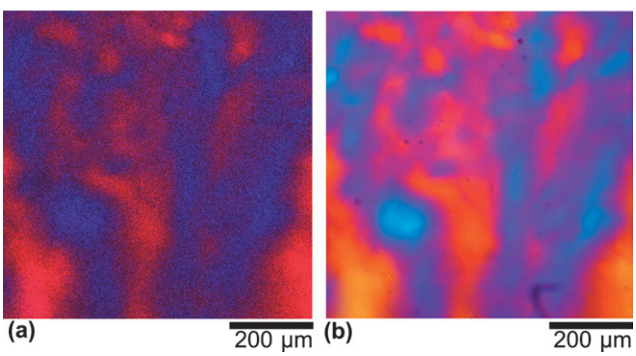

Fig. 3 The nematic phase visualized with (a) the combined setup, using only the blue and red light channel of the confocal detector and (b) a Nikon Coolpix 995 camera with the complete visible wavelength range. Domains with different retardation colours represent different director orientations of the nematic phase. Comparison of the two images demonstrates that the confocal detector gives a reliable representation of the director orientations.

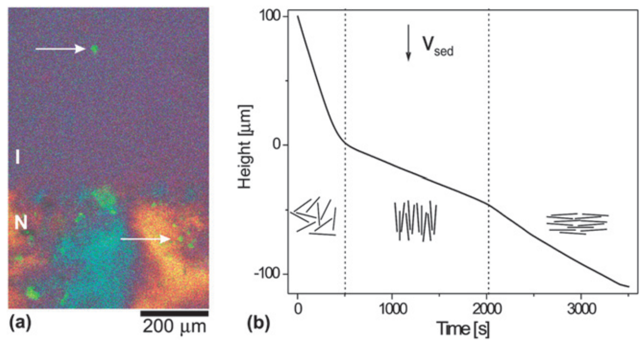

Fig. 4 (a) Fluorescent tracer sphere (indicated with a white arrow) sedimenting through the isotropic phase (I) towards the nematic phase (N). The green dots in the nematic phase are also sedimenting tracer spheres, one of which is also indicated with a white arrow. Due to the retardation filter used (OPD = 530 nm) the isotropic phase appears purple. The nematic phase displays several colours depending on the orientation of the director. (b) The time dependent height of a tracer sphere as it sediments through the isotropic phase and two different domains in the nematic phase.

viscosity calculated from the sedimentation velocities of a set of falling spheres is 2.7 (± 0.3) Pa s for motion along the director and 1.4 (± 0.2) Pa s for motion perpendicular to the director. Consequently, the Stokes friction factor is two times larger for the parallel than for the perpendicular direction ($f_\parallel/f_\perp = 1.9$), in contrast to experiments on thermotropic liquid crystals ($f_\parallel/f_\perp = 0.63$ and 0.52)[5,6] and theory ($f_\parallel/f_\perp = 0.50$–0.67).[4] The latter results, however, pertain to Ericksen numbers much smaller than 1, where viscous forces are much weaker than elastic forces. The Ericksen number is defined as the ratio of viscous ($\eta v/a$) and elastic forces (K/a^2): $Er = \dfrac{\eta v a}{K}$ with η the viscosity, v the sedimentation velocity, a the sphere radius, and K a Frank elastic constant.[12] For our system of colloidal rods we have $\eta = 2$ Pa s, $v = 5 \times 10^{-8}$ m s^{-1}, and $a = 5 \times 10^{-6}$ m. For boehmite rods there are no K values available, but based on the values of the colloidal rod systems tobacco mosaic virus[13] and FD-virus,[14] we estimate $K \approx 2.5 - 5 \times 10^{-13}$ N. This results in a value for the Ericksen number of 1 to 2, which means that viscous forces are of the same order as the elastic forces. Computer simulations by Araki and Tanaka[15] reveal that for Ericksen numbers of about 1 the particle motion changes in character and that for increasing Ericksen numbers the difference between $f_{\parallel}$ and $f_{\perp}$ decreases, but in all cases $f_{\parallel}$ is smaller than $f_{\perp}$. Since the Ericksen number scales like the cube of the radius of the sedimenting sphere, a simple way to test the hypothesis that the special effects are due to the Ericksen number, would be to use a smaller sedimenting sphere. So far we have not performed such experiments.

The combination of fluorescent confocal and polarization microscopy is a powerful technique for investigation of local rheology and its dependence on the director field. It is in principle also suitable for thermotropic liquid crystals and for diffusion coefficient measurements. Unlike existing techniques our technique does not require a uniform director field but instead enables the measurement of local orientation dependent rheology and domain boundaries within a single experiment.

The challenge is now to relate these Stokes friction factors to the fundamental viscous properties of a colloidal liquid crystal system.[16] While simulations have been performed,[15] theory on the direction dependence of Stokes drag in the Ericksen number around 1, the regime relevant to our experiments, is still lacking.

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