Rotation of a sphere in a viscoelastic liquid subjected to shear flow. Part II. Experimental results

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Synopsis

The effect of the viscoelastic nature of the suspending medium on the rotation of spherical particles in a simple shear flow is studied experimentally using a counter-rotating device. To evaluate the effect of variations in rheological properties of the suspending media, fluids have been selected which highlight specific constitutive features. These include a reference Newtonian fluid, a constant viscosity, high elasticity Boger fluid, a single relaxation time wormlike micellar surfactant solution, and a broad spectrum shear-thinning elastic polymer solution. It is shown that particle rotation slows down, when compared to the Newtonian case, as elasticity increases, in qualitative agreement with computer simulation studies. Despite the variation in constitutive properties and the wide range of time scales of the fluids, it is found that the Weissenberg number suffices to scale the data: the dimensionless rotation speed of the spheres in the different fluids scales onto a single master curve as a function of the Weissenberg number. This indicates that the

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I. INTRODUCTION

In many technological applications, particles are dispersed in fluids that display a complex rheological behavior, as exemplified by filled polymers, nanocomposites, paints, and consumer-care products [e.g., Hornsby (1999); Barnes (2003)]. Suspending solid particles in rheologically complex fluids further complicates their rheological behavior. The rheological properties of a suspension depend, to a large extent, on the relative motions of the particles and on their subsequent hydrodynamic interactions. Whereas the individual motions of particles and their resultant rheological behavior in Newtonian fluids under flow are well understood [e.g., Batchelor (1974); Brenner (1972); Goldsmith and Mason (1967), Happel and Brenner (1991); Jeffrey and Acrivos (1976); Liu and Masliyah (1996)], this is not the case for particles in viscoelastic fluids.

As the flow-field around a particle is transient in nature in a Lagrangian sense [e.g., Happel and Brenner (1991)], rheologically complex fluids with time dependent and non-linear viscoelastic properties can be expected to lead to differences in the velocity and pressure field with respect to the Newtonian case. As a consequence, the particle motions and the hydrodynamic interaction between particles will change. This leads to differences in rheological properties and microstructure development. At low to moderate volume fractions, the relation between shear stress \( \sigma \) and shear rate \( \dot{\gamma} \) of suspensions of particles in complex fluids remains similar to that of their matrix fluids [Ohl and Gleissle (1993)]. The shear stress-shear rate master curves can be obtained with shift factors \( B_{\sigma} \) defined as

\[
B_{\sigma}(\phi) = \left( \frac{\dot{\gamma}(\phi = 0)}{\dot{\gamma}(\phi)} \right)_{\sigma=\text{constant}}
\]

with \( \phi \) the particle volume fraction. The shift factors \( B_{\sigma} \) can be interpreted as internal shear rate amplification factors in the matrix due to the presence of rigid particles and are sometimes observed to be different from the Newtonian case [Ohl and Gleissle (1993)]. The changed hydrodynamic effects imply that the analytically derived Einstein [Einstein (1906, 1911)] and Batchelor [Batchelor and Green (1972)] equations for the viscosity valid at low particle concentrations, or the empirical Krieger-Dougherty equation [Krieger and Dougherty (1959)] for the viscosity valid for all concentrations, cannot be expected to hold for flows at higher elasticity. Moreover, in some cases shear-thickening is observed at relatively low volume fractions for suspensions of particles in Boger fluids [Sciocco et al. (2005)]. In order to obtain predictive equations for \( B_{\sigma} \), the effects of the viscoelastic nature of the medium need to be understood. The first and second normal stress differences as function of the shear stress for the suspensions keep the overall shape similarity with these functions for the matrix fluids, but they do not scale as expected by the shear stress-equivalent internal shear rate concept [Ohl and Gleissle (1993)]. The first normal stress difference is generally found to be positive and decreasing [Mewis and de Bleyser (1975)], and the second normal stress difference negative and increasing (in magnitude) with increasing volume fraction [Mall-Gleissle et al. (2002)].

Some intriguing features of particles suspended in viscoelastic fluids, also pointing to complex effects of matrix viscoelasticity are the observations of particle migration under influence of normal stress differences [e.g., Karnis and Mason (1966); Highgate (1966)]; the observation of rod-dipping for highly concentrated suspensions with a Boger fluid as matrix in contrast to rod-climbing as observed for low concentrations and the pure fluid [Zarraga et al. (2001)]; and the formation of specific microstructures for particles dis-
persed in viscoelastic fluids such as particle chain formation [Michele et al. (1977)], which is found to have a subtle dependence on the rheological properties of the suspending medium [Scirocco et al. (2004)]. To get better understanding of the behavior of particles in complex fluids more fundamental studies are required. The motion of single particles in viscoelastic media under flow is far from understood, even for non-Brownian, spherical particles at low concentrations and in shear flow [e.g., Larson (1999); Barnes (2003)]. There has been a specific interest, mostly from computational rheology, in the sedimentation of a single particle in viscoelastic fluids, which is a benchmark problem for viscoelastic fluids [e.g., Harlen (2002)].

The main focus in this paper is on the rotation speed of a single, non-Brownian sphere in simple shear flow. In a Newtonian fluid in shear flow, the rotation speed \( \omega \) (rad/s) of a single, spherical particle in the bulk, in absence of inertia, Brownian motion, and gravity, and with the no-slip boundary conditions imposed on the surface of the sphere, is given by the undisturbed fluid vorticity [Einstein (1906, 1911); Jeffery (1922)]:

\[
\omega = \frac{\dot{\gamma}}{2}
\]

with \( \dot{\gamma} \) the macroscopic shear rate (s\(^{-1}\)). The rotation speed of the particle is independent of the particle radius and the viscosity of the fluid. This theoretical prediction has been verified directly for the first time by Trevelyan and Mason in 1951, although it was already inferred from intrinsic viscosity measurements by Vand (1948). Cox et al. (1968) calculated the streamlines around a sphere in shear flow in a Newtonian fluid analytically and verified the calculations using experiments. In Fig. 1(a) the streamlines in the vorticity plane are shown. Due to the linearity of the governing equations, there is a perfect symmetry of the lines across both the flow and the velocity gradient directions. Poe and Acrivos (1975) studied the effects of fluid inertia on particle rotation in a Newtonian fluid in shear flow experimentally and showed that the dimensionless angular velocity decreases with increasing Reynolds number. Mikulencak and Morris (2004) studied the effects of fluid inertia on particle rotation in a Newtonian fluid numerically; also here, the spheres were shown to slow down at higher particle Reynolds numbers as compared to the inertialess solutions. When comparing the calculated streamlines for the case with fluid inertia to the case without, the effect of inertia was to break the for-aft symmetry of the streamlines across the velocity gradient direction. Mikulencak and Morris (2004)
suggested that this leads to a lower torque on the particle and, as such, a slowing down of the particle relative to the inertialess case.

The flow-field around the particle is transient in nature in a Lagrangian sense: an individual fluid element goes through a complex and time-dependent deformation along its trajectory past a particle. Combined with the time dependence and the rheologically nonlinear response of the suspending fluids, this will lead to deviations from the Newtonian solution. The first experimental studies by Bartram et al. (1975), Gauthier et al. (1971a), and Gauthier et al. (1971b) revealed no difference with the Newtonian case, which can be attributed to the fact that the measurements were limited to fluids and conditions where elastic effects were still weak. More recently Astruc et al. (2003) presented experimental results on particle rotation in viscoelastic media, and although there is large scatter on the data and the Weissenberg number was defined in a nonclassical manner as \( Wi(\gamma_1) = G'(\omega_1)/G''(\omega_1) \), the trend in the data is that particles slow down due to the elasticity of the medium, when compared to the Newtonian case. From the theoretical side, there are analytical studies where the stress tensor of a dilute suspension of spheres in a viscoelastic fluid is calculated [e.g., Greco et al. (2005, 2007); Koch and Subramanian (2006)]. In these studies, the results are limited to the second-order fluid limit and no difference with the Newtonian case is predicted for the particle rotation speed. Subramanian and Koch (2007) calculated the streamlines around a sphere in shear flow in a second-order fluid analytically and found that the symmetry along the flow and velocity gradient directions is broken, due to the elasticity. A computer simulation study of this problem by Hwang et al. (2004), which gives direct results for the rotation speed of a single particle in a viscoelastic fluid, shows that the elasticity of the fluid slows the rotation of the particles down, unfortunately their results are limited to the two-dimensional case. As general conclusion from all these studies, one can qualitatively say that particles tend to slow down in viscoelastic fluids as compared to the Newtonian and second-order fluid cases and the higher the elasticity, the more the particles slow down. A recent full 3D computational study by D’Avino et al. (2008) gives quantitative results for the rotation speed of a sphere in a viscoelastic fluid under shear. Different constitutive models are used (Bird-Carreau, upper-convected Maxwell, Phan-Thien-Tanner, and Giesekus) in the simulations and the results are compared. Except for the Bird-Carreau model, where no elasticity nor time effects are present, all models result in a slowing down of the rotation of the sphere and the sphere slows down most as a function of the Deborah number \( De = \tau \dot{\gamma} \) [with \( \tau \) the relaxation time (s)] when the upper-convected Maxwell model is used. In Fig. 1(b) the effects of the viscoelasticity on the streamlines in the vorticity plane are shown [D’Avino et al. (2008)]. The streamlines are shown for a Giesekus model (\( \alpha = 0.2 \)) in shear flow at \( De = \tau \dot{\gamma} = 1.0 \). When comparing Fig. 1(a) with Fig. 1(b), or the Newtonian with the viscoelastic case, respectively, it is clear that the for-aft symmetry is broken due to the elasticity of the medium. For the viscoelastic case, the streamlines become tilted and two zones appear where there is fluid backflow.

In the present work, the rotation speed of non-Brownian spheres will be studied experimentally. A number of model suspending fluids, selected to highlight specific constitutive features, have been selected, prepared, and characterized. These fluids include a Newtonian liquid, a constant viscosity, elastic Boger fluid, a shear-thinning viscoelastic polymer solution, and a single relaxation time wormlike micellar surfactant solution. Spherical particles of polystyrene and glass, in a size range between 50 and 200 \( \mu m \), have been dispersed in these fluids. Their motion is studied using videomicroscopy in combination with a counter-rotating plate-plate rheometer.
II. MATERIALS AND METHODS

A. Rheometry

The linear and nonlinear viscoelastic properties were measured with two ARES strain-controlled rheometers (TA instruments, Newcastle DE), one equipped with a sensitive 100 g/(g cm) transducer, the other one with a 2000 g/(g cm) transducer. All measurements were performed using cone and plate geometries [diameter (mm)/cone angle (rad): 25/0.04, 25/0.01, 50/0.02, and 50/0.04]. Different cone angles and diameters were used to check for wall slip and to rule out the presence of elastic instabilities. Temperature was controlled by means of a fluids bath or Peltier element, and temperature in the fluid in the gap was measured by using an external calibrated miniature thermocouple (hypodermic needle probe, Omega, Stamford CT). Temperature variations were found to be smaller than 0.2 °C in all cases. Aging of the fluids was checked by measuring their rheology at different times with at least 3 weeks in between. Measurements were done in a range of temperatures from 10 °C to 40 °C and time-temperature superposition was used to calculate master curves.

B. The counter-rotating rheometer combined with videomicroscopy

The rotation speed of a particle in shear flow is measured by means of digital videomicroscopy using a custom made counter-rotating rheometer (see Fig. 2). The counter-rotating device is composed of two stress controlled rheometers: a Physica MCR-300 for driving the top geometry and a Physica DSR-300 for controlling the bottom geometry (Paar Physica, Austria). These rheometers were delivered with special firmware and can be independently controlled. A BK7 glass parallel plate geometry with a diameter of 50 mm is used as flow geometry, in combination with an in-house developed glass cup that surrounds the bottom plate, which prevents lower viscosity samples from flowing out. The presence of the cup renders the velocity profile three dimensional near the outer edge. To evaluate the importance of the effect in our case, the numerical calculations of Vrentas et al. (1991) for a Newtonian fluid in such geometry were used. Their calculations predict a critical radius $r_c$, defined as the radial distance from the midpoint of the geometry (see Fig. 2) in the middle of the gap, where the deviation of the velocity from the ideal parallel plate velocity field [Eq. (3)] without cup is 1%, of around 21 mm for a
gap of 3 mm. Within this radius the velocity field is equal to the ideal velocity field within 1%. Since the rheometer is counter-rotating, there is a stagnation plane with velocity zero in between the glass plates. The position of this zero-velocity plane can be shifted up and down using a potentiometer, which adjusts the rotation speed of the bottom and top plate, while keeping the relative velocities and hence the shear rate constant. As such it is readily possible to capture a particle and keep it in the field of view of the microscope. The optical setup is composed of a Wild M5A stereomicroscope (Heerbrugg, Switzerland), with a maximum magnification of $50 \times (1.59 \pm 0.01 \, \mu m/pixel)$, connected to a Basler A301-fc digital camera (80 frames/s, 8 bit, resolution $658 \times 494$, progressive scan). This enables one to record sequences of images using Streampix software (Norpix, Canada). The microscope/camera is mounted on high resolution lab-jacks (High Load Lab Jacks, model 271, Newport, RI) via low vibration rods (Heavy Duty Rod Systems, model 45, Newport, RI), which assure reproducible and accurate positioning. By using a cylindrical lens directly focusing the microscope into the gap, the motion of particles in the vorticity plane can be observed. The images recorded in this way are, however, slightly deformed. Using a prism and going through the top plate (as in Fig. 2), the motion in the velocity gradient plane can be measured. The latter configuration, combined with a diffuse lighting system, yielded the most accurate measurements.

The macroscopic shear rate of the fluid in a parallel plate geometry is given by

$$\dot{\gamma}(r) = \frac{\omega_R r}{h}$$

with $\omega_R$ the relative angular velocity of the plates with respect to each other, $r$ the radial position, and $h$ the gap (see Fig. 2). The error on the shear rate for a particle in the rotational rate measurements is dependent on errors in each of these factors. Errors in the angular velocity $\omega_R$ are determined by the torque resolution of the DSR-rheometer and can be neglected compared to errors in the other two parameters. The radial position $r$ of the particles is determined by means of a grid, printed on an overhead transparency, which is placed between the cup and the bottom plate. After a measurement on a particle is done, the microscope is focused on the grid and the position of the particle with respect to the grid is recorded. The position of the grid with respect to the inner opaque part of the geometry is then determined. The diameter of this part, which consists of PVC, is known with an accuracy of 0.1 mm by measurement with a marking gauge. Using this method one can measure the radial position of the particle in the geometry with an accuracy better than 200 $\mu m$. This accuracy results in an error in the shear rate of about 1% in all cases.\footnote{Radial migration of a particle is not considered here, only the accuracy of the apparatus.} The particles were typically situated at radial positions between 15 and 19 mm. The lower limit of 15 mm comes from the geometry, which is not transparent at smaller radial positions; the upper limit of 19 mm is restricted to avoid the effect of 3D flow near the cup [Vrentas et al. (1991)].

The gap $h$ is set by the rheometer after setting the zero gap. The error in the gapsetting itself is estimated to be 1 $\mu m$. The setup is located in an air-thermostated room but no additional temperature control is available and, as such, temperature could have an effect on the gapsetting. The error arising from temperature variations on the gap height was tested to be about 3.1 $\mu m/°C$. As such this effect is negligible for the measurements reported here because of the large gaps and small temperature variations ($25 \pm 5 \, °C$). Gaps of 3–5 mm, which are large with respect to the particle diameter, were used in all measurements to avoid wall effects. Care has been taken to limit the measurements to
particles situated near the middle of the gap, not next to the upper or lower plate. Bikard et al. (2006) showed using numerical simulations that, in a Newtonian fluid, the rotation speed of a sphere suspended in the middle between two parallel plates moving in opposite directions coincides with the well-known free body, unconfined result [Eq. (2)] for gaps larger than five times the particle diameter. In the present work, care was taken to make sure that this condition was met. In most measurements, the particles are at least ten times the particle diameter away from the wall. A few series of systematic measurements to check the dependence of rotation on the position of the particle in the gap showed that this dependence was absent in our experiments. Confinement effects and wall effects have not been studied yet. The presence of wall slip on the glass plates has been checked using measurements of the rheological properties at different gaps: no measurable slip length could be determined.

As already mentioned, the setup is located in an air-thermostated room but there is no additional temperature control. The temperature in the room itself can vary slightly (±0.5 °C); viscous heating and heat from the light sources used as condensors can have an effect on the rheological properties of the fluid in the gap. To minimize the effect of temperature on the final results of the rotation speed of particles, the temperature of the fluid in the gap was measured by using an external calibrated miniature thermocouple (hypodermic needle probe, Omega, Stamford CT) after each experiment. This made it possible to correct the experimental data on the rotation speed of particles for temperature variations and reduce the scatter in the data using the shift factors $a_T$ of the time-temperature superposition of the rheological data.

The objective of each experiment is to obtain the period of rotation of a single individual particle. The particle concentration in the suspensions needs to be kept low, to avoid interaction with nearby particles. The particle concentration in the suspensions was very inhomogeneous, because a small amount of particles was mixed into the suspending medium to create the suspension before closing the gap of the rheometer. After the loading, one particle was selected and moved, by shearing, to a desired isolated position, at least five times the particle diameter away from all other particles. For each fluid-particle size combination, measurements were done on a series of particles, as such not focusing on a single particle which could have important defects that influence the rotation. For each fluid-particle size combination, at least five different particles were selected. In general 10–25 different particles were studied.

The recorded images were analyzed using ImageJ [Abramoff et al. (2004)]. The motion of spots on a particle were monitored and the period of rotation could be determined by comparing images: after one period of rotation the image of the particle has to be identical to the image made before the rotation, meaning that the spots have to be at the same position on the particle in both images. The accuracy of this analysis is set by the time between images and its magnitude relative to the period of rotation; in experiments performed at low shear rates (<0.1 s$^{-1}$), a frame rate of 0.5 images/s was sufficient; at higher shear rates, the frame rate was increased to 5 images/s to increase accuracy. The maximum error induced by the time between the images in the experiments is 5% in three isolated cases; in general, the error induced in this way is <1%. To get an accurate measure for the period of rotation and to be able to detect steady-state, an averaging over at least ten periods was performed in all cases. The final period of rotation reported is an average over all steady-state periods of rotation.

C. Particles

Particles of different sizes and surface properties were used. The different sizes allow us to evaluate possible wall slip effects at the fluid-particle surface. Studying chemically
different particles is helpful to exclude fluid-particle interaction effects, like adsorption. An overview of the particles is given in Table I. To study particle rotation we have to be able to visualize something on or in the particles. The glass particles have optical imperfections [see Fig. 3(a)]. These imperfections can be scratches on the surface as well as inclusions of air inside the particle. These points of reference enable us to follow the rotation of the particle, by determining when they return at the exact same position after one full rotation of the particle. The PS particles, on the other hand, do not have any optical imperfection. Therefore, these particles are coated on one side to create Janus-particles. Titanium and gold coatings were applied using physical vapor deposition. A combination of titanium and gold is found to yield the most homogeneous coatings [see the SEM image in Fig. 3(b)]. First, the particles are deposited as monolayer on a hydrophobic glass plate. Upon evaporation of the solvent, the glass plate with the particles is brought under vacuum and a piece of titanium followed by a small piece of gold are evaporated above the particles. Next, the particles are recovered from the glass plate by ultrasonincating in an apolar solvent, isopropanol (IPA). Finally, the IPA is removed by evaporation and one ends up with dry, half-coated polystyrene particles [see the SEM image in Fig. 3(b)].

D. Suspending media and their rheological behavior

A Newtonian reference fluid, a dilute polymer solution with a nearly constant viscosity (a “Boger fluid”), a shear-thinning elastic polymer solution, and a viscoelastic wormlike micellar surfactant solution were used as suspending media. The experimental require-

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter (µm)</th>
<th>Standard deviation (µm)</th>
<th>Obtained as</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>49</td>
<td>0.8</td>
<td>aqueous suspension</td>
<td>Duke Scientific</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>150</td>
<td>4.5</td>
<td>aqueous suspension</td>
<td>FLUKA</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>200</td>
<td>3</td>
<td>aqueous suspension</td>
<td>FLUKA</td>
</tr>
<tr>
<td>Glass</td>
<td>~160–190</td>
<td>...</td>
<td>powder</td>
<td>Flex-o-Lite</td>
</tr>
</tbody>
</table>

FIG. 3. (a) Optical microscopy picture of a glass particle (diameter 170 µm) and (b) ESEM picture of a half coated polystyrene particle (diameter 50 µm).
ments for the fluids were that they needed to be transparent, stable, with zero-shear viscosities above 5 Pa s to prevent flow out of the gap or problems with sedimentation on the timescale of the experiments. For practical purposes, zero-shear viscosities were best below 100 Pa s, to avoid problems with loading. The fluids were also chosen to highlight specific constitutive properties and their properties will be described in detail.

The elasticity of the viscoelastic media is characterized with a dimensionless Weissenberg number defined as

\[ \text{Wi}(\dot{\gamma}) = \frac{N_1(\dot{\gamma})}{\sigma_{xy}(\dot{\gamma})} \]  

with \( N_1 \) the first normal stress difference (Pa), \( \sigma_{xy} \) the shear stress (Pa) and \( \dot{\gamma} \) the shear rate (s\(^{-1}\)).

1. **The Newtonian fluid**

As Newtonian fluid a low molecular weight polyisobutylene (Parapol 1300 - Exxon Chemical) was used, as supplied. No significant normal stress differences nor shear-thinning could be detected in the experimental shear rate window (0.01–50 s\(^{-1}\)) and no significant value of the storage modulus could be measured in dynamic oscillatory tests (frequency window: 0.01–100 rad/s). At 25 °C the viscosity \( \eta \) is 83 Pa s. The temperature dependence of the viscosity could be fitted with the following Arrhenius relation:

\[ \ln(\eta) = \frac{7918}{T} - 22.14 \]  

with \( T \) the temperature in Kelvin. The activation energy \( E_a \) obtained is 65.8 kJ/mol.

2. **The Boger fluid (BF)**

As Boger fluid a solution of 2000 ppm (by weight) Oppanol B200 (PIB) with a mean viscosimetric molecular weight of 4.10\(^6\) (BASF) in a low molecular weight PIB, Infineum S1054 (Exxon Chemical), was selected. The solvent used to prepare the Boger fluid is 2-chloropropane (Fluka). The preparation procedure is as follows:

- First, the high molecular weight PIB is dissolved in an excess of chloropropane (~5 wt % PIB) using a magnetic stirrer at room temperature, until the solution is homogeneous. This took as long as 2 weeks. The low molecular weight PIB is also dissolved in chloropropane; an excess chloropropane is not needed in this case.
- Then, the two solutions of PIB/chloropropane are poured together and again the resulting solution is stirred for a few days.
- Next, the chloropropane is removed from the solution using a ROTAVAP with temperatures up to 50 °C and a final vacuum of less than 1 mbar. The complete removal of chloropropane took up to a week. Subjecting only the matrix fluid to the same treatment yielded no measurable change in the viscosity [Scirocco (2004)].

The rheological behavior of this fluid is shown in Fig. 4. The linear viscoelastic storage and loss moduli are shown in Fig. 4(a), using time-temperature superposition to a reference temperature of 25.1 °C. The linearity limit was measured using a strain sweep and a linearity limit of about 0.3 strain units was observed. All data in Fig. 4(a) are well in the linear regime. The terminal low frequency region is reached. The nonlinear steady-state viscosity \( \eta(\dot{\gamma}) \) and Weissenberg number [Eq. (4)] as a function of shear rate are shown as master curves at 25.1 °C in Fig. 4(b). To determine the time to reach steady-
state, step rate experiments have been performed and the transient data showed that steady-state was reached after about 300 s (order of magnitude). This time was set as delay time in the steady-state experiments and the data were checked later with a slightly higher delay time. At shear rates above 3 s⁻¹, a viscoelastic instability, previously reported by several authors [e.g., Calado et al. (2005); Magda and Larson (1988)], was observed. The onset of this instability could be easily observed since it resulted in a jump in the apparent viscosity and the apparent first normal stress difference.

The shift factors $a_T$ needed to calculate the master curves are calculated on the basis of the measured zero-shear viscosities and the curves are shifted accordingly. The zero-shear viscosities $\eta_0$ as a function of temperature $T$ are fitted according to the Arrhenius relation:

$$\ln(\eta_0) = \frac{8116}{T} - 23.32.$$ (6)

The activation energy $E_a$ obtained is 67.5 kJ/mol, which is essentially the activation energy of the pure solvent. The zero-shear viscosity at 25 °C is 50 Pa s. Also shown in Fig. 4(b) is a least-square fit of the Weissenberg number with the following best fit function:

$$Wi = -0.95 + 15(1 - \exp(-0.47 \dot{\gamma})),$$ (7)

which is only expected to be valid in the shear rate region where experimental data are present ($\dot{\gamma}=0.40–3.2$ s⁻¹). This function is used later, to determine the Weissenberg number which corresponds to the macroscopic shear rate working on the rotating particle in the counter-rotating device.

3. The shear-thinning elastic polymer solution (ST)

For a shear-thinning elastic fluid a solution of 11 wt % of a high molecular weight PIB (MW$_v$=1.2·10⁶, Sigma-Aldrich) in Pristane (Sigma-Aldrich) was used. This fluid is a home made version of the NIST standard reference material [Schultheisz and Leigh (2002)]. The dissolution process of the PIB took about 3–4 months, as initially determined by simple observation of optical density differences and later by measuring the rheology data with at least 3 weeks in between.
The rheological behavior for this fluid is shown in Fig. 5. The linear oscillatory data are shown as master curves using a reference temperature of 24.7 °C in Fig. 5(a). A linearity limit of about 0.5 strain units was measured. The terminal low frequency region is reached. The nonlinear steady-state viscosity $\eta(\dot{\gamma})$ and Weissenberg number $Wi(\dot{\gamma})$ are shown as master curves in Fig. 5(b). To determine the steady-state, step rates have been performed. It was shown that steady-state was reached after about 10 s, which agrees with the largest relaxation time observed in the linear viscoelastic data. For larger cone angles and higher shear rates, edge fracture developed [Larson (1992)]. Edge fracture set the limit to the highest shear rate that could be reached in the measurements. The shift factors $a_T$ needed to calculate the master curves are obtained from the measured zero-shear viscosities $\eta_0$ and the curves are shifted accordingly. The Arrhenius relation used is

$$\ln(\eta_0) = \frac{3837}{T} - 8.533.$$  

The activation energy $E_a$ obtained is 31.9 kJ/mol. The zero-shear viscosity at 25 °C is 77 Pa s. A least-square fit of the Weissenberg number as a function of shear rate using the following best fit function yields [see Fig. 5(b)]:

$$Wi = -0.20 + 0.86 \dot{\gamma}^{0.36},$$

which is only valid in the shear rate region where experimental data are present ($\dot{\gamma} = 0.40–160$ s$^{-1}$). This function is again used later, to evaluate the Weissenberg number which corresponds to the macroscopic shear rate, acting on the rotating particle in the counter-rotating device.

4. The wormlike micellar solution (WMS)

As viscoelastic surfactant solution, a solution of 100 mM CetylPyridiniumChloride (CPyCl, Merck), 60 mM SodiumSalicylate (NaSal, Fluka), and 100 mM SodiumChloride (NaCl, Fisher scientific) in demineralized, double distilled water was used following Miller and Rothstein (2007) and Rehage and Hoffmann (1988). This fluid is a wormlike micellar solution and the linear viscoelastic rheological behavior can be modeled fairly
well with only one relaxation time [Rehage and Hoffmann (1988)]. The composition is chosen to avoid problems with shear banding as much as possible, following the formulations of Miller and Rothstein (2007).

The linear viscoelastic properties are shown in Fig. 6(a) using a reference temperature of 25.0 °C. A linearity limit of about 0.2 strain units was observed. The terminal low frequency region is reached. The lowest temperature tested was 19.6 °C; no measurements were done at lower temperatures because of a phase transition. This phase transition resulted in different rheological behavior and the fluid became opaque (white). The steady-state viscosity $\eta(\dot{\gamma})$ and Weissenberg number $Wi(\dot{\gamma})$ are also shown in Fig. 6(b). Steady-state was reached after about 5 s (order of magnitude). The measurements were done under different geometries (cone and plates with different cone angles and diameters). In these kinds of solutions, shear banding may occur [Miller and Rothstein (2007)]. The composition of the fluid is chosen to avoid these problems as much as possible, however, at the higher shear rates ($>3 \text{ s}^{-1}$), the flow-field does become inhomogeneous, as can be inferred from a shear stress versus shear rate plot (not shown here) by a leveling off of the flow curves at the higher rates (maximum in the stress) and from the observation that data obtained with different geometries no longer superimpose perfectly [see Fig. 6(b)]. Starting from a shear rate of 3 s$^{-1}$, the fluid probably displays shear banding. In the experiments for the rotation speed we limited us to data below this shear rate.

The shift factors $a_T$ needed to calculate the master curves are calculated on the basis of the measured zero-shear viscosities and the curves are shifted accordingly. The Arrhenius relation used is

$$\ln (\eta_0) = \frac{15925}{T} - 50.09.$$  

(10)

The activation energy $E_a$ obtained is 132 kJ/mol. At 25 °C the zero-shear viscosity is 28 Pa s. A least-square fit of the Weissenberg number gave as best fit [see Fig. 6(b)]

$$Wi = 0.056 + 0.82\dot{\gamma}^{1.14},$$  

(11)

which is only valid in the shear rate region where experimental data are present ($\dot{\gamma} = 1.4–19 \text{ s}^{-1}$).
E. Comparison between the different fluids

In Table II a comparison is made between the constitutive properties of the different fluids. BF, ST, and WMS stand for Boger fluid, shear-thinning elastic polymer solution, and wormlike micellar surfactant solution, respectively. The reference temperature is 25.0 °C. The zero-shear viscosity $\eta_{\dot{\gamma} \to 0}$ is compared to the low frequency limit of the norm of the complex viscosity $|\eta^*|_{\omega \to 0}$. The largest difference between the two viscosities is observed for the Boger fluid where the difference is less than 5%. The dominant relaxation times $\tau$, based on the linear viscoelastic data, are defined as the inverse of the crossover frequency $[G'(\omega_{\text{cross}})=G''(\omega_{\text{cross}})]$; $\tau=1/\omega_{\text{cross}}$. The activation energies scaled with the ideal gas constant $R$ are shown. The limiting low frequency values for the first normal stress coefficient are defined as $\Psi_{\text{osc}}^{\text{1}}=\lim_{\omega \to 0}(2G'/\omega^2)$. A comparison with the nonlinear flow data are not given in this case, since the limiting values are not reached in those experiments as the normal forces fall outside of the measurement range of the transducers. Finally, the power-law exponent $n$, as calculated by fitting $\eta=K(\dot{\gamma})^{-n}$ to the viscosity data in shear rate regions relevant for the experiments on particle rotation (for ST: 1–10 s$^{-1}$ and for WMS: 1–3 s$^{-1}$), is shown and is a measure for the degree of shear-thinning of the fluid.

### III. EFFECTS OF BROWNIAN MOTION, INERTIA, AND GRAVITY

Since our objective is to study hydrodynamic, viscoelastic effects, one wants to exclude effects of Brownian motion, inertia, and sedimentation. Particle inertia slows the rotation of the particles down in Newtonian fluids when compared to the inertialess case [Mikulencak and Morris (2004)], therefore it has to be carefully considered as the effect of viscoelasticity on the rotation speed is expected to be similar and of similar magnitude [Astruc et al. (2003); D’Avino et al. (2008)]. Before presenting any experimental results on particle rotation, in this section the importance of these phenomena in the worst possible experimental situations encountered is assessed.

The Peclet number $Pe$, a measure for the importance of viscous forces as compared to Brownian forces, should be larger than 1 to be in a hydrodynamically dominated regime. The Peclet number is defined as

$$Pe = \frac{\eta \dot{\gamma} a^3}{kT}.$$  \hspace{1cm} (12)

The worst case scenario encountered is PS spheres with radius $a=25$ μm in the wormlike micellar solution at very low shear rates $\dot{\gamma}=0.01$ s$^{-1}$ when the fluid viscosity $\eta = 28$ Pa s. With $k$ the Boltzmann constant and $T$ the temperature (298 K), the Peclet number is of order $O(10^6)$, which is much larger than 1. As such, it can be concluded that Brownian motion is not important, even at the lowest rates.

### TABLE II. Comparison between the different fluids; for explanation, see text.

| Fluid | $\eta_{\dot{\gamma} \to 0}$ (Pa s) | $|\eta^*|_{\omega \to 0}$ (Pa s) | $\tau$ (s) | $E_{\text{a}}/R$ (K) | $\Psi_{\text{osc}}$ (Pa s²) | $n$ |
|-------|-----------------|-----------------|---------|-----------------|----------------------|------|
| BF    | 49.7            | 52.1            | no crossover | 8116          | 520                  | 0    |
| ST    | 76.6            | 76.5            | 0.05     | 3837           | 113                  | 0.3  |
| WMS   | 27.7            | 27.9            | 0.83     | 15925          | 52                   | 0.7  |
The particle Reynolds number Re, a measure for the relative importance of inertial forces compared to viscous forces, should be much smaller than 1, to be in the viscous dominated regime. A generalized Re number for shear-thinning fluids can be defined as

\[ \text{Re} = \frac{\rho_s \gamma a^2}{\eta(\gamma)} . \]  

(13)

The worst case scenario for this number is glass particles with radius \( a = 100 \mu m \) in the shear-thinning elastic polymer solution at high shear rates \( \gamma = 6 \text{ s}^{-1} \) when the fluid viscosity \( \eta(\gamma) = 36 \text{ Pa s} \). With the fluid density \( \rho_s = 800 \text{ kg/m}^3 \), the generalized Reynolds number is of order \( O(10^{-6}) \), which is much smaller than 1. As such, one can conclude that inertial effects are expected to play no role [Mikulencak and Morris (2004)].

Finally, the worst case scenario for sedimentation is for glass particles with radius \( a = 100 \mu m \) in the wormlike micellar surfactant solution. The sedimentation speed \( u_0 \) of a single particle in a viscous fluid is calculated as follows:

\[ u_0 = \frac{2(\rho_p - \rho_s)g a^2}{9 \eta} = 5.9 \text{ mm/h} \]

(14)

with \( g = 9.81 \text{ m/s}^2 \), the particle density \( \rho_p = 2500 \text{ kg/m}^3 \), the fluid density \( \rho_s = 1000 \text{ kg/m}^3 \), and the fluid viscosity at the relevant shear rate of \( \eta = 20 \text{ Pa s} \). As such, sedimentation is at first glance an effect that could have some importance on the flowfield around the particle. However, when calculating the sedimentation speed of a PS particle \( (\rho_{\text{PS}} = 1054 \text{ kg/m}^3) \) instead of a glass particle \( (\rho_{\text{glass}} = 2500 \text{ kg/m}^3) \) under otherwise identical conditions, the speed is about 30 times lower. Since results of the glass particles and polystyrene particles fall together on a single curve, the effect of sedimentation is neglectable.

### IV. EXPERIMENTAL RESULTS

#### A. The Newtonian fluid

A Newtonian fluid was studied at first, to verify whether the well-known result for the rotation speed of a particle in a Newtonian fluid under shear flow could be reproduced and to test the accuracy of the measurements. The rotation speed \( \omega \) for 50 \( \mu m \) spherical PS particles as a function of shear rate is shown in Fig. 7. A least-square fit through the data points results in the following relationship:

\[ \omega_E = (0.493 \pm 0.008) \gamma - (0.002 \pm 0.006), \]

(15)

which is in good agreement with the theoretical prediction [Eq. (2)]. The relative error, defined as \( (\omega_T - \omega_E) / \omega_T \), with \( \omega_T \) the theoretical Newtonian rotation speed at the measured shear rate [Eq. (2)] and \( \omega_E \) the experimental speed, for each experimental data point, is at most 7%. The error bars on the data points, shown in Fig. 7, are based on the standard deviation on the periods of rotation of a particle that result from the image analysis and have an error of at most 17%. These variations in the periods of rotation are caused by additional experimental artifacts such as slight deviations from the spherical shape of the particle, the effects of hydrodynamic interaction with incidentally passing particles, small flow irregularities, and small radial movement and cross-stream migration of the particle. However, the mean value of the rotation speed differs less than 7% from the theoretical value. The horizontal error bars are not shown. As discussed in Sec. II, the error in the shear rate is about 1% in all cases.
B. The Boger fluid

Data on particle rotation obtained during startup in the Boger fluid at different shear rates are shown in Fig. 8. Since it is not possible to obtain instantaneous information about the rotation speed, the data points in the graph are an average rotation speed over a time period of one period of rotation. Each data point is then put in the middle of this time interval. The dashed lines in the graph indicate the values taken as steady-state mean.
values. The full lines in the graph are least-square fits with damped oscillatory functions and are meant as guides to the eye. A damped oscillatory behavior can be clearly observed, with the oscillations becoming more pronounced as the shear rate is increased. A particle is observed to rotate faster than the steady-state mean value right after start-up. After this, the particle slows down before eventually reaching its steady-state. This damped oscillatory behavior was also observed in the simulations of D’Avino et al. (2008). As shown in Fig. 8, steady-state rotation speeds are only reached after ~300 s for this fluid (much longer than for the other fluids) and this steady-state value can still vary and slowly drift due to the effects of hydrodynamic interaction with incidentally passing particles and cross-stream migration of the particle. Care has been taken to make sure steady-state, and not start-up, rotation speeds are used in plotting the steady-state data in Fig. 9. This was most critical for the Boger fluid as compared to the other fluids, since in that case the time to reach steady-state was at least ten times longer.

Experimental steady-state results on the rotation speed of coated PS spheres of 50 μm and glass spheres of ~170 μm as a function of the macroscopic shear rate on the particle in this fluid are shown in Fig. 9 along with the theoretical Newtonian no-slip limit. In Fig. 9(a) the absolute rotation speed ω is plotted as a function of the shear rate. In Fig. 9(b) the rotation speed divided by the shear rate is shown as a function of the shear rate. The latter way of plotting the data shows the deviations from Newtonian behavior more clearly and provides us with a dimensionless scale for the rotation speed. The error bars on the data points are based on the standard deviation on the periods of rotation of a particle that result from the image analysis and, as suggested in a previous paragraph, are an overestimation of the error in the average rotation speed.

Figure 9 gives the angular velocity and scaled angular velocity of a particle as a function of the macroscopic shear rate in the Boger fluid. At higher shear rates where the elasticity sets in, the particles slow down when compared to the Newtonian case. Radial cross-stream migration of the particles under the influence of normal stress differences limited extending the measurements to higher shear rates. The rotation data on the large glass particles and the smaller PS particles cannot be distinguished from each other. The only difference is that the rotation speed of the PS particles could be measured up to higher rates, because migration phenomena only came into play at higher rates as compared to the glass particles, which have a larger diameter.
C. The shear-thinning elastic polymer solution

Experimental results of the scaled rotation speed of coated PS spheres of 50 \( \mu m \) as a function of the macroscopic shear rate on the particle are shown in Fig. 10(a) along with the Newtonian no-slip limit. The error bars on the data points are based on the standard deviation on the periods of rotation of a particle. It can be concluded that, once again, for the shear-thinning fluids a slowing down of the particles at higher rates is observed when compared to the Newtonian case. The onset of an elastic instability, along with migration of the particles, puts a limit on the highest measurable rates.

D. The wormlike micellar surfactant solution

Experimental results on the scaled rotation speed of coated PS spheres of 50, 150, and 200 \( \mu m \) as a function of the macroscopic shear rate on the particle are shown in Fig. 10(b) along with the Newtonian no-slip limit, confirming the trend of slowing for the other viscoelastic fluids. Migration of the particles puts a limit on the highest measurable rates. Since this fluid is water based and as such evaporation is a problem, measurements were done using an in-house developed glass solvent trap, which was mounted over the parallel plate geometry. As discussed in Sec. II D, there are some issues with inhomogeneous flow (shear banding) at shear rates above 3 s\(^{-1}\) in cone and plate geometries. The shear rates at which measurements on particle rotation are done are limited to shear rates below 2 s\(^{-1}\), where no inhomogeneous flow has been observed in the rheological characterization of the fluids. The results shown in Fig. 10(b) are also obtained on particles situated at different positions, both height and radius, in the geometry and the results for the rotation speed scale together on a single curve, which also rules out the presence of inhomogeneous flow. There was also no visual color change or optical inhomogeneity of the fluid apparent during any of the experiments.

V. Comparison between the results and discussion

To compare the results in the different fluids, the rotation speed and the scaled rotation speed are calculated as a function of the Weissenberg number [Eq. (4)]. This is done using the least-square fits of the Weissenberg number \( Wi(\dot{\gamma}) \) with the best fit functions [Eqs. (7), (9), and (11)]. Equation (7) for the Boger fluid is used in the shear rate range...
from 0.23 s$^{-1}$ up to 0.84 s$^{-1}$, Eq. (9) for the shear-thinning elastic polymer solution in the range from 0.032 s$^{-1}$ up to 6.1 s$^{-1}$, and Eq. (11) for the wormlike micelle solution in the range from 0.56 s$^{-1}$ up to 1.1 s$^{-1}$. As such, the best fit equations are slightly extrapolated from their strict validity ranges, which are obtained from the experimental steady-state rheology data of the fluids. For the Boger fluid and the shear-thinning elastic polymer solution the extrapolation is minimal, for the wormlike micelle solution the extrapolation is somewhat more severe, and the error on the Weissenberg number can be expected to be slightly larger. The resulting graphs, obtained using the curve fits, are shown in Fig. 11 where the rotation data for the three different fluids are compared. In Fig. 11(a) the rotation speed and in Fig. 11(b) the rotation speed scaled with the shear rate are shown as a function of the Weissenberg number. The error bars and the different particle sizes have been omitted in the plots for clarity. To prevent severe extrapolation of the best fit functions, a number of data points have been omitted in the low shear rate/Weissenberg limit. This is most severe for the Boger fluid. For the shear-thinning polymer solution and the wormlike micellar surfactant solution the loss of data points in the low Weissenberg limit is not a big issue because the Newtonian limiting law is almost reached [see Fig. 11(b)], but for the Boger fluid, this is not the case. When comparing the results, one can see that rotation data could be recorded up to higher elasticities in the Boger fluid compared to the wormlike micellar solution and shear-thinning polymer solution. This is because migration set in much slower in the first as compared to the latter two. This might perhaps be linked to the higher viscosity of the Boger fluid as compared to the viscosities of the other fluids at the relevant shear rates. Figure 11(a) shows the large differences in absolute rotation speed of the particles in the different fluids. The total range of measured rotation speeds covers almost three decades. Figure 11(b) shows that the data for the different fluids scale on a single master curve (within experimental error) when the scaled rotation speed of the particle $\omega/\dot{\gamma}$ is plotted against the Weissenberg number $Wi(\dot{\gamma})$. Although, when looking at a fixed Weissenberg number in Fig. 11(b), the rotation in the wormlike micellar solution seems to slow down more, this difference is well within experimental error.

The scaling onto a single curve, when plotting the scaled rotation speed data as a function of the Weissenberg number, is quite successful. This is somewhat surprising as the Weissenberg number reflects a dependency on the normal stresses differences relative to the shear stress, and normal stresses cannot affect the rotation rate directly. Yet the simple scaling seems to be general, indicating that the indirect effect of normal stresses
on the rotational behavior of the spheres is most important. In the computer simulation studies of D’Avino et al. (2008), transient start-up data on the particle rotation speed also pointed to a major role for the first normal stress difference as the rotation speed of the particle became steady-state at nearly the same strain as the first normal stress difference.

The fluids used cover a broad range of relaxation times (see Table II) and the nonlinear viscoelastic time effects in the suspending fluids do not seem to play a direct role. This can be rationalized by the fact that for the shear stress components acting on the particle surface, the time effects slow down the shear stress build-up and decay with respect to the Newtonian case [see Fig. 1(b)]. This means that the point at which the tangential shear stresses start to exert a torque on the particle surface would be “delayed,” but also the point where the stresses significantly decay would shift further on the particle surface. As net effect this does not lead to a direct change in the rotation speed of the particle, only the streamlines become slightly tilted as is shown in Fig. 1(b). The effect of viscoelasticity hence seems to be an indirect one and is related to how the disturbance pressure and velocity fields are altered. The scaling with the Weissenberg number suggests that the normal stresses strongly influence the pressure and velocity fields around the particle, inducing a breaking of symmetry with respect to the Newtonian case as can be concluded from comparing Figs. 1(a) and 1(b). Consequently, the normal stress effects will profoundly change the streamlines, the local velocities, and the deformation rates close to the particle surface, bearing some similarity with the effects of fluid inertia on particle rotation [Mikulencak and Morris (2004)].

In Fig. 12 a comparison between simulations and experiments using the Weissenberg number as a measure for the elasticity, defined as in Eq. (4), is shown. The parameters of the constitutive models used in the simulations (single mode Giesekus and upper-convected Maxwell model) are not fitted to the rheological data of the fluids, and the rotation speed of the particles still shows a similar behavior as experimentally observed. This is somehow surprising given the simulation results as reported by D’Avino et al. (2008) (see Fig. 2 and 4 in that paper), where different rheological models with different
characteristics concerning first normal stress coefficient, shear-thinning, and second normal stress coefficient resulted in qualitatively and quantitatively different rotation speeds as a function of the Deborah number, defined as \( \text{De} = \tau \dot{\gamma} \) (with \( \tau \) the relaxation time). In the present work, however, using the Weissenberg number [Eq. (4)] instead of the Deborah number, the differences between the simulation results using different constitutive models become less pronounced. This is because the effects of shear-thinning and multiple relaxation times are fully covered by the Weissenberg number as defined in Eq. (4), while this is not the case for the Deborah number. For example, for the Giesekus model the first normal stress coefficient shear-thins faster as a function of shear rate than the viscosity and as such the Weissenberg number will show shear-thinning, too, while the Deborah number will remain a linear function of the shear rate. Note also that, while the upper-convected Maxwell model resulted in the largest slowing down effect as a function of the Deborah number [D’Avino et al. (2008)], this is not the case as a function of the Weissenberg number (see Fig. 12), where the slowing down effect is shown to be smaller for the upper-convected Maxwell model as compared to the Giesekus model.

The relative insensitivity of the particle rotation on the details of the rheological behavior of the suspending media is in strong contrast with the remarkable sensitivity of the particle chaining [Scirocco et al. (2004)] and some of the rheological properties such as the unexpected shear thickening in filled Boger fluids [Scirocco et al. (2005)]. For these phenomena a scaling of the effects with the Weissenberg number was not possible. However, for these phenomena the interactions between particles are important, not just single particle behavior. For the case of particle chaining, for example, Michele et al. (1977) observed that the particles inside a chain did not rotate during shear flow. As such, there might not be a direct relation between the single particle problem studied here and chaining, where particle interactions are clearly important. Based on these arguments, one can expect that the details of the rheology of the fluids become important when particles interact. Future work should hence focus on visualizing the streamlines around a single particle or considering the hydrodynamic interactions between two particles.

VI. CONCLUSIONS

The effect of medium viscoelasticity on the rotational velocity of a sphere in simple shear flow was studied in different fluids: a Newtonian fluid, a Boger fluid, a shear-thinning elastic polymer solution, and a wormlike micellar surfactant solution. In all viscoelastic fluids a slowing down of the particle rotation is observed, relative to the Newtonian case. The rate of rotation, rendered dimensionless by the shear rate, can be scaled onto a master curve with the Weissenberg number as the only governing parameter. For Boger fluids, some transient results could be obtained which reveal a damped oscillatory response of the rotation speed. The experimental results compare well with numerical simulations, even when considering the difference between the rheological models used in the simulations with different characteristics concerning first normal stress coefficient, shear-thinning, and second normal stress coefficient.

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