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String formation in sheared suspensions in rheologically complex media: The essential role of shear thinning

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Synopsis

When particles are dispersed in a rheologically complex medium, a striking alignment of particles into strings can be observed during shear flow. This occurs even under conditions where the suspensions would be considered to be dilute. However, a conclusive explanation for the specific role of the rheological properties of the suspending medium has not been given since the phenomenon was first discovered, now around 40 years ago. The present work aims to elucidate the role of the fluid properties as well as the effect of geometrical conditions by performing experiments, which separate the different factors that could play a role in string formation. First, the presence of significant normal stress differences is shown to help, but it is not a necessary condition for string formation. Second, moderate confinement is shown to be enhancing alignment as well. Third, shear thinning and its effect on lubrication forces are identified to be the crucial factor for alignment. In particular, shear thinning allows to maintain the individual rotation of each particle in a string. This is a requirement to meet the zero torque condition; otherwise, the string would tumble as a whole. In confirmation of this it is observed that when small particles are added as depleting agent to push larger particles closer together, at a critical concentration the flow induced alignment is suppressed. Particle doublets and triplets are then observed to rotate as a whole and tumble on drifting Jeffery orbits ending up in a log-rolling state, oriented along the

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vorticity direction. The suppression of the string formation upon increasing attraction confirms that enabling the rotation of the separate particles within the string is crucial for maintaining the structure aligned in the flow direction. This suggests that the pertinent rheological parameters of the suspending fluids are those related to the lubrication flows occurring in the gap, i.e., the overall level of the viscosity and the amount of shear thinning.
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INTRODUCTION

Many user products are soft matter composites, which consist of particles dispersed in a rheologically complex fluid. The presence of these particles further complicates the flow behavior of the fluids. Hydrodynamic interactions between the particles have a considerable effect on the rheological characteristics of the suspension while these interactions are at the same time also being influenced by the complex fluid properties. This causes the study of particle interactions in viscoelastic fluids to be challenging. To optimize end-properties and production processes, however, a fundamental understanding of particle dynamics in various liquids at different environmental conditions is required, a problem which has been approached both experimentally and theoretically.

The importance of rheological effects on interactions between particles becomes clear when studying for instance sedimentation. While in a Newtonian fluid particles move away from each other during sedimentation [Batchelor (1982)], they are attracted to each other and align in a non-Newtonian fluid [Riddle *et al.* (1977)]. An alignment of particles can also be induced in simple shear flow, as first observed by Michele *et al.* (1977). The same authors also reported that particles separate into different chains according to their size [Michele *et al.* (1977)]. Recent observations show even higher order organisation of particle strings in viscoelastic media, when sheared for very long times, in the form of two-dimensional crystalline structures, as observed by Pasquino *et al.* (2010a).

Normal stress differences were first suggested to be the main cause for alignment. It was even suggested that a critical Weissenberg number (*Wi*), defined as the first normal stress difference over the shear stress, controls the alignment [Michele *et al.* (1977); Lyon *et al.* (2001)]. Giesekus (1978) suggested that spatial variations in normal stress differences "push" the particles together. The lubrication flow, which slows down the liquid in the gap and reduces the local shear rate, causes a difference in the normal stress differences in and outside the gap, and this has been suggested to lead to chaining. The arguments by Giesekus (1978) were stated even stronger by Joseph, in terms of a compressive viscoelastic pressure [Joseph and Feng (1996)]. Joseph and coworkers argued that an experimentally observed effect of shear thinning on chain formation was explained by the fact that shear thinning leads to much stronger local velocity gradients which amplify the normal stress effects [Joseph (1996); Huang *et al.* (1998)].

Experiments on suspensions of particles in Boger fluids, i.e., fluids with elastic properties and a constant viscosity, were a crucial test for this hypothesis. Won and Kim (2004) performed experiments on monolayers in a Boger fluid whereas Scirocco *et al.* (2004) studied alignment in bulk in a similar fluid. Won and Kim (2004) observed an ordered zig-zag structure, but the spacing between the particles stayed too large to obtain strings. The zig-zag structures can also be obtained in confined suspensions in purely Newtonian media [Cheng *et al.* (2011)]. Scirocco *et al.* (2004) did not observe any alignment of particles in sheared Boger fluids in bulk, even for ratios of the elastic to the viscous forces as high as 200. Scirocco *et al.* (2004) also explored a wider range of fluids, with shear thinning and varying elastic properties. A more subtle dependency of string formation on the rheological properties of the suspending fluid then hitherto reported was observed, with both elasticity and shear thinning contributing. The time dependency of string formation was also studied in the quest for clues to the formation mechanism, showing that string formation could be very slow. The results suggest that the alignment was not controlled by an internal time scale of the suspending fluid. These phenomena have been studied in more detail using microscopy techniques, and it was recently shown that the kinetics of string formation also reveal a strong dependence on the rheological details of the suspending medium [Pasquino *et al*. (2013); Mirsepassi *et al*. (2012)]. The microscopy observations show that the influence of wall effects and migration also seems to be very system dependent. Pasquino *et al*. (2013) showed that, for suspensions with matrices based on hydroxypropylcellulose in water, migration and chaining compete whereas Mirsepassi *et al*. (2012) did not observe any migration effect when the medium was a polyethylene oxide solution of similar rheology. Interestingly, recent work using trajectory analysis on two interacting particles in different viscoelastic fluids showed that, in the range of shear rates probed, no aligned particle pairs could be found [Snijkers (2009); Snijkers *et al*. (2013)] whereas more concentrated suspension do show aligned strings at similar conditions. This suggests that a certain degree of confinement or concentration may help.

Apart from the long particle trains in the flow direction, vorticity oriented doublets or triplets can be observed, for example, when particle size is reduced, and (probably attractive) colloidal interactions become important [Pasquino *et al*. (2010b)]. Joseph (1996) argued that such structures can also be formed when inertial properties dominate normal stress effects. Vorticity orientation is also observed in a range of shear rates when shearing a suspension of ellipsoidal particles embedded in a viscoelastic fluid [Gunes *et al*. (2008)].

Numerical simulations have also been used to study the chaining and vorticity alignment. Within the realm of continuum mechanics, Hwang and Hulsen (2011) presented a systematic study for a Giesekus and a Leonov fluid and observed a typical transition from random organised particles over an initial clustering to fully developed string formation as the solvent viscosity lowers and the Weissenberg number increases. They also studied the effect of shear thinning and, in agreement with experiments, found shear thinning to ease the formation of strings. They also concluded that it remained difficult to quantify the effect of shear thinning on string formation. Hwang and Hulsen (2011) also showed that the angular velocity of particles in a string was reduced, which holds clues as to how the particles obey the zero torque condition. Continuing with the continuum models, Choi and Hulsen (2012) looked in more detail at the string characteristics and showed that as the Weissenberg number increases, particles can form longer strings. Moderate wall confinement promotes the alignment of particles, but too strong confinement hinders the alignment by enhancing repulsive interaction between particles. However, the simulations by Hwang and Hulsen (2011) and Choi and Hulsen (2012) were 2D only, and the streamlines for cylinders differ quite strongly for those of spheres, even in the Newtonian case. The case of 3D simulations has so far only been carried out for two particles in an Oldroyd-B fluid [Yoon *et al*. (2012)].

Santos de Oliveira *et al*. (2012) used a mesoscopic simulation method called responsive particle dynamics and simulated particles with a diameter not much larger than the diameter of the radius of gyration of the dissolved polymer. Their results suggested that the chaining occurs because of a change in polymer density before and behind the particles, i.e., a shear induced depletion effect. However, Santos de Oliveira *et al*. (2012) disallowed rotation of the particles, which means that it is not clear how the zero torque balance on the particles is satisfied. Also, as the authors point out the mechanism invoked to explain the chaining, this requires for larger colloids (relative to the radius of gyration of the polymer) to be very close to each other, which is not in agreement with microscopic observations [Scirocco *et al.* (2004)], where larger particle spacings are clearly observed.

Overall, the experimental results reveal a subtle dependence on the rheological properties of the suspending medium. These trends are confirmed by the 2D simulations, although the 2D nature of the simulations makes a direct comparison with experiments difficult. The focus of earlier work has been on understanding how and why particles come together on the basis of an imbalance in normal stress differences, which is said to be amplified by shear thinning. Santos de Oliveira *et al.* (2012) have put forward an explanation based on depletion and a shear induced attractive force, which can be interrogated experimentally.

In the present work, the mechanisms responsible for alignment in sheared viscoelastic fluids will be further evaluated experimentally. First, we will revisit the proposed role of normal stress differences as a necessity for string formation, as discussed in literature [Michele *et al.* (1977); Lyon *et al.* (2001); Giesekus (1978); Petit and Noetinger (1988); Won and Kim (2004)], by attempting to induce alignment in a fluid without significant normal stresses but with relatively strong shear thinning. We will also visualise the trajectories of non-Brownian spheres while they approach to form a string in a wormlike micellar fluid to investigate if they are really pushed together, which is the question most prior research (including our own) has focused on. Second, we will investigate the effect of confinement on alignment as it is believed that this is very beneficial for alignment [Pasquino *et al.* (2010b)]. Third, a number of experiments are performed to answer a possibly more relevant question, i.e., why the particles do not tumble once they come together. We try to understand, in particular, how the zero torque condition is satisfied by particles, which are in a string. For this, the rotation of the particles in a string as well as the effects of a depletant pushing the particles closer together are studied in order to evaluate the local force and torque balances experimentally.

MATERIALS AND METHODS

Materials

The model suspension for the experiments consists of 40 μm diameter polystyrene (PS) particles (Dynoseeds, Microbeads AS, Norway) at a fixed concentration of 0.7 wt. %. These particles were chosen because their size allows easy visualization with an optical microscope while sedimentation is not a problem as it occurs on timescales much larger than the experimental ones. An estimate for the sedimentation velocity is given by

$$U = \frac{2(\rho_p - \rho_f) g r^2}{9\eta}, \tag{1}$$

with ρ_p the density of the particles, ρ_f the density of the fluid, r the radius of the particles, g the gravitational acceleration, and η the medium viscosity. For aqueous suspensions, the sedimentation speed obtained this way is 0.063 mm/h. The weight fraction of 0.7 wt. % is within a semidilute regime, which allows easy visualization but sufficient encountering possibilities between particles. This concentration is similar to others used in literature to study alignment, e.g., Pasquino *et al.* (2010a) and Won and Kim (2004).

A wormlike micellar solution (WMS) was prepared by adding 100 mM of cetylpyridinium chloride (CPCl, Merck, Germany), 60 mM of sodium salicylate (NaSal, Fluka, Switzerland), and 100 mM of sodium chloride (NaCl, Thermo Fisher Scientific, USA) to milli-Q water and homogenizing for 1 h in an ultrasonic bath. The solution is stored for at least 2 days at room temperature before use, to allow complete homogenization. The specific composition was chosen to minimize the occurrence of shear banding, as stated by Miller and Rothstein (2007). The rheological properties of fluid chosen here can be well described using a single relaxation time Giesekus model. This specific solution has often been used as a model fluid in literature, e.g., by Pasquino *et al.* (2010a) and Snijkers *et al.* (2013). To induce depletion interactions to the large particles dispersed in this medium, poly-methylmethacrylate (PMMA) spheres with a diameter of 6 μm (Spheromers CA6) from Microbeads were added in a range of concentrations from 0.1 to 1 vol. %.

As a second dispersion medium, a *fd*-virus suspension was prepared. *fd*-Virus was prepared and purified according to standard biochemical protocols and using the XL-1 blue strain of *Escherichia coli* as the host [Sreeprasad *et al.* (2008)]. The suspension was made by adding 2 mg/ml of *fd*-virus to a Tris-HCl buffer, containing 20 mM of Tris in Milli-Q water. Both Tris and HCl were obtained from Sigma-Aldrich (USA). Additionally, polyisobuten (PIB) in heptane was made by adding 3.5 wt. % of PIB to the solvent and letting it dissolve during 2 days on a magnetic stirrer. All the chemicals were obtained from Sigma-Aldrich (USA). Finally, a 5 wt. % Polyethyleneoxide (PEO) in water solution was prepared. Polyox WSR (water-soluble resin) 1105 with a molecular weight of 900 000 g/mol from Dow (USA) was used. The polymer is added to water at an intermediate rate while stirring magnetically. Adding it too slowly leads to a fast viscosity buildup, which prohibits complete dissolution; adding polymer too quickly, on the other hand, causes clumping. It took 5–6 days for the Polyox to completely dissolve.

Rheological properties of the suspending media were measured using an ARES-G2 strain-controlled rheometer from TA Instruments (Delaware, US), combined with cone and plate geometries with a diameter of 50 mm and an angle of 0.02 or 0.04 rad. The exact amount of fluid required to fill the gap was added to avoid imprecisions due to scraping. Temperature control was performed using a Peltier element, limiting temperature variations to $\pm 0.1\,^{\circ}$C. The rheology of the *fd*-virus suspension was characterized using a Physica MCR-501 stress-controlled rheometer (Anton Paar, Austria) and different geometries. The most relevant rheological properties of the fluids are shown in Fig. 1. The fluids exhibit similar zero shear viscosities. The power-law indices are 0.08 for the

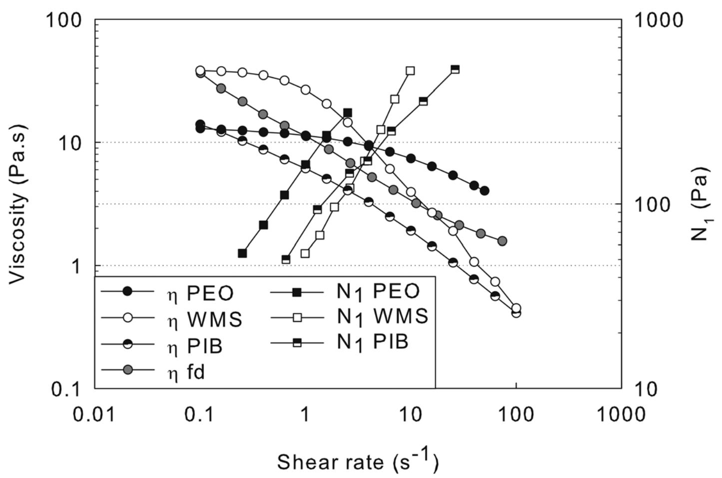

FIG. 1. Viscosity (η) and first normal stress difference (N_1) as a function of shear rate for two polymer solutions (PEO, PIB), a wormlike micellar surfactant solution (WMS) and a *fd*-virus suspension, as described in the text. All fluids show significant shear thinning behavior. For the *fd*-virus solution, no normal stresses could be measured, neither using ARES-G2 nor MCR 501.

WMS, 0.34 for the PIB solution, 0.57 for the *fd* suspension, and 0.65 for the PEO solution. These values are indicative for the *fd* since the zero shear viscosity could not be established for this fluid. No measurable normal stress differences could be detected for the *fd*-suspensions whereas the PIB, PEO, and WMS solutions had significant first normal stress differences as indicated in Fig. 1.

Methods

To investigate particle trajectories, a counterrotating setup was used. This instrument combines two stress-controlled rheometers: a Physica MCR-300 and Physica DSR-300 that are used for driving, respectively, the upper and lower geometry (Anton Paar, Austria). The setup has been described earlier by Snijkers (2009). By letting both geometries rotate in opposite directions, a stagnation plane is created between them. The position of this plane can be adjusted by varying the relative rotating speeds of both geometries using a potentiometer while keeping the total shear rate constant. A transparent parallel plate (Anton Paar, Austria) as well as a Couette geometry (Hellma, Germany) have been used, the former creating a horizontal stagnation plane and the latter a cylinder-shaped stagnation plane. The Couette has a gap of 7.76 mm between the inner cylinder with a radius of 25 mm and the outer cylinder with a radius of 32.76 mm. Temperature control is performed by placing the instrument in a thermostated room (25 °C) and measuring the temperature in the sample before and after each experiment with an external thermocouple (Omega, Stamford, USA). The stagnation plane can be visualized both in the velocity gradient en vorticity direction, using an optical setup consisting of a Wild M5A stereomicroscope (Heerbrugg, Switzerland) and a Basler A301-fc digital camera. The software used to acquire the images is Streampix (Norpix, Canada) and ImageJ (Open source software, National Institutes of Health, USA) was used for image processing. For image analysis such as particle tracking MATLAB (Mathworks, USA) was used.

EXPERIMENTAL

Flow induced structures for different suspending media: General observations

Various fluids with shear thinning and elastic properties cause alignment of suspended particles, as illustrated in Fig. 2. Figure 2(a) shows strings in the bulk of a CPCl wormlike micellar fluid. Figure 2(b) shows strings formed in a solution of PIB in heptane, again focusing on a plane in the bulk of the sample. This observation differs from the outcome of the simulations by Santos de Oliveira *et al.*, who used responsive particle dynamics simulation method (RaPiD) and modelled this particular suspending medium [Santos de Oliveira *et al.* (2011)]. In the polymer solution, the simulations predict that the particles remain randomly dispersed, which is not observed here. For the wormlike micellar system, on the other hand, Santos de Oliveira *et al.* (2011) do observe the formation of strings in the flow direction at shear rates higher than $2\,s^{-1}$. Strings in a water-based polymer solution are shown in Fig. 2(c). It should be noted that the images in Fig. 2 all represent pseudo-steady state situations as strings tend to come together laterally to form two-dimensional sheets or bundles eventually. Long shearing times of the order of several hours are required to obtain this, the exact value depending on parameters such as shear rate and fluid properties.

The question we would like to address here is whether normal stress differences are a necessary condition for string formation. While it has been shown that shearing a

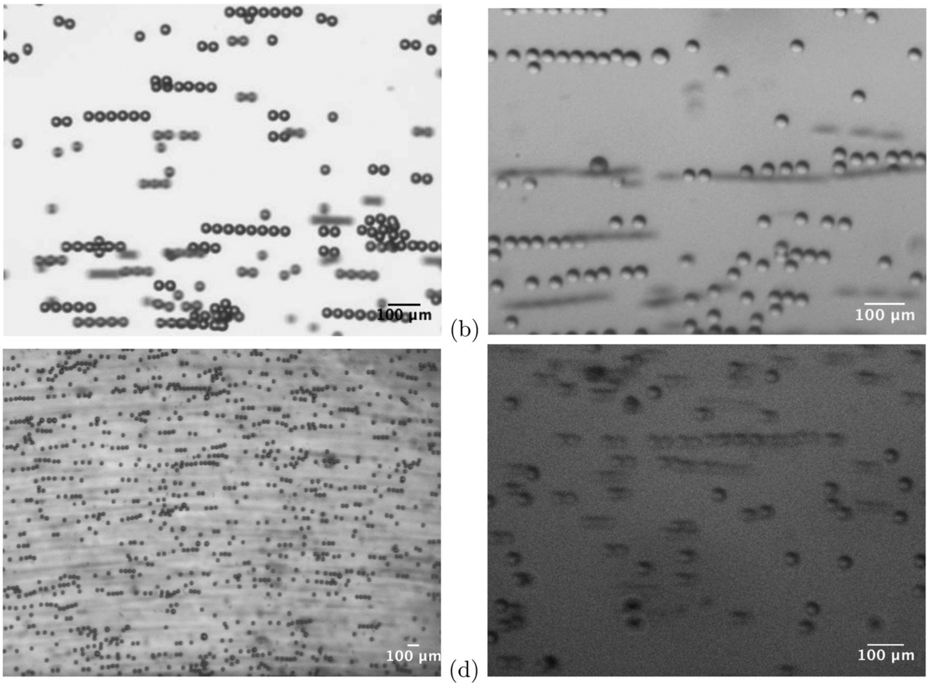

FIG. 2. String formation of 40 μm PS spheres at 0.7 wt. % in various viscoelastic suspending media: (a) Wormlike micellar solution of CPCl in water, $\dot{\gamma} = 4\ s^{-1}$, (b) polymer solution of PIB in heptane, $\dot{\gamma} = 6\ s^{-1}$, (c) viscoelastic polymer solution of PEO in water, $\dot{\gamma} = 6\ s^{-1}$, (d) a shear thinning *fd*-virus solution $\dot{\gamma} = 10\ s^{-1}$. The gap was 1 mm in each experiment, and the field of view was placed approximately in the center between the parallel plates, to see bulk phenomena without effects of the presence of walls.

suspension of particles in an elastic Boger fluid does not lead to string formation [Scirocco *et al.* (2004)], this is not a proof normal forces are not required. We therefore evaluate the suggested role of the normal stress differences for particle chaining [Michele *et al.* (1977); Lyon *et al.* (2001); Giesekus (1978); Won and Kim (2004)]. It was investigated if chain-like structures could be induced in a suspension of large PS particles in a suspension of *fd*-virus particles. For this inelastic suspension, no first normal stress differences could be measured within the resolution limit of $\mathcal{O}$ (1) Pa of the rheometer/geometry combination. Even assuming the presence of normal forces just below the detection limit, the *Wi* for the situation depicted in Fig. 2(d) is below 0.12, based on a shear stress of around 33 Pa at a shear rate of 10 s^{-1}. However, as shown in Fig. 2(d), strings are produced here, despite the lack of normal force differences in the medium. It should be noted that the dominating rheological property of this fluid is its shear thinning behaviour. The presence of strings shows that significant normal stress differences are not a necessary condition for string formation. The strings are not very well defined and take several minutes to form. This is contrary to the WMS, where string formation starts almost instantaneously, suggesting that normal forces, while not being a necessity, can still promote string formation.

Approach trajectories

To further investigate the effect of normal stress differences, the approaching motion of two particles, which initiates the formation of a string, is studied. Using quantitative video-microscopy and particle tracking, the motion upon joining is monitored in different planes parallel to the flow direction vector. For this, a counterrotating parallel plate geometry is used to investigate a suspension of 40 μm PS spheres in a WMS. Looking through the upper plate and focusing on particles close to or within the stagnation plane, a clear view can be established of the movements of the particles in the velocity gradient plane.[1] This is depicted schematically in Fig. 3(a). The stagnation plane was kept in the center of the gap to study bulk effects without interaction with the walls. The location of each particle in each frame is identified using in-house built MATLAB routines, with which their trajectories can be reconstructed based on the algorithm developed by Crocker and Grier (1996), as shown in Fig. 3(b). For a Newtonian fluid the displacement in this plane should be zero if the particles are situated on the same streamline (not shown). However, a cross stream line migration is observed [Fig. 3(c)]. The motions in the vorticity plane can be monitored by looking at the gap between the plates from the side, as shown

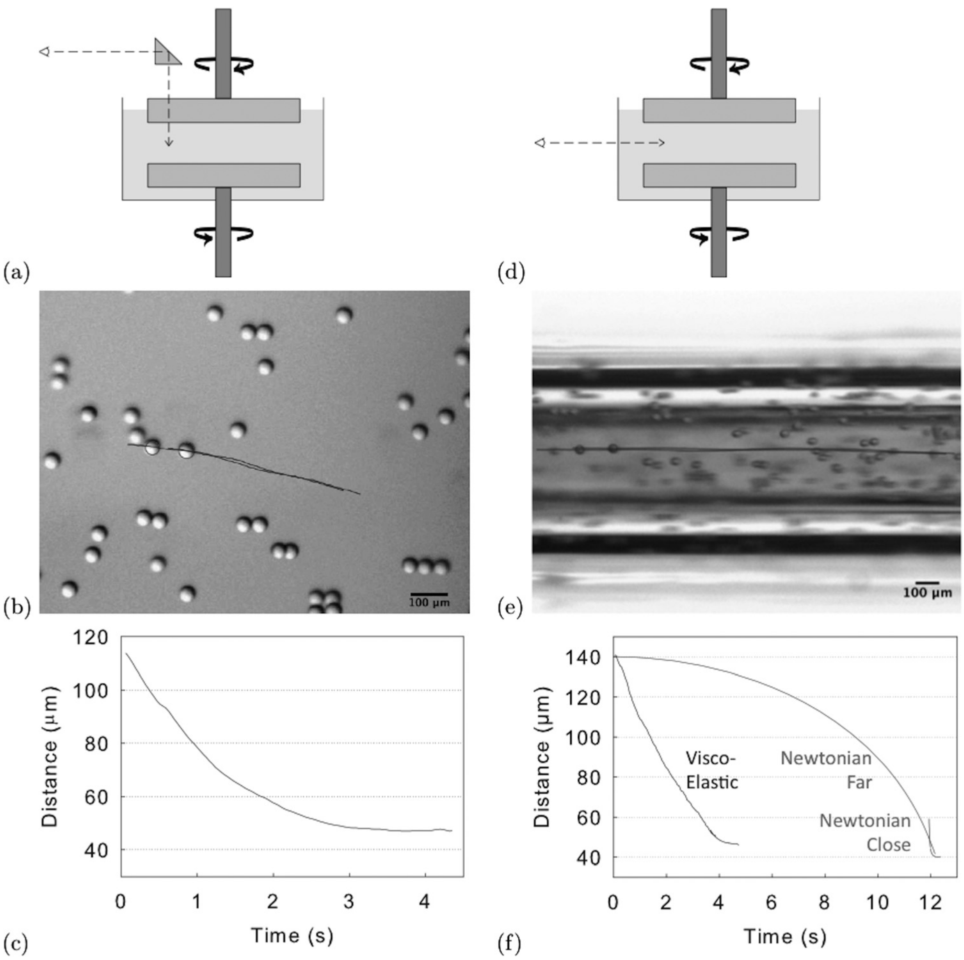

FIG. 3. (a) Schematic description of the velocity gradient plane setup. (b) Top view: Trajectories of two joining particles overlaid onto the picture displaying one of their first positions (velocity gradient plane at $\dot{\gamma} = 4.2\ \mathrm{s}^{-1}$). (c) Time evolution of the interparticle distance in the vorticity plane. (d) Schematic description of the vorticity plane setup. (e) Side view: Trajectories of two joining particles overlaid onto the picture displaying one of their first positions. ($c = 0.35$ wt. % and $\dot{\gamma} = 6\ \mathrm{s}^{-1}$). (f) Time evolution of the interparticle distance between two particles in the velocity gradient plane, experimental for CPCl in water and theoretically calculated for a Newtonian solvent under similar shear conditions in a lubrication approach and using a far field solution.

schematically in Fig. 3(d). Representative particle trajectories are shown in Fig. 3(e). Figure 3(c) shows how the particle separation distance typically decreases in the velocity gradient plane. Figure 3(f) shows how the particles migrate towards each other in the vorticity plane. This observed approaching motion in the WMS can now be compared to the situation for particles in a Newtonian fluid. Figure 3(f) compares the experimental result to the calculation for two force-free 40 μm particles approaching each other in a Newtonian fluid, which is sheared at the same shear rate with the particles starting off with a distance of 140 μm between them and an offset of 5° across the velocity gradient direction. These parameters were chosen to mimic the experimental starting situation. This result was obtained following the approach by Russel *et al.* (1989). The transition between the far field and lubrication solutions is set at a distance of 55 μm between the centers of the spheres. More explanation can be found in the Appendix. The experimental graph consists of two different joining motions combined since particles did not stay in the field of view long enough to monitor the entire trajectory.

The approaching curves in Fig. 3 in comparison to the predictions for the Newtonian case allow to draw some qualitative conclusions. First, the approaching speed in the WMS is more or less constant before the lubrication zone is entered. No strong acceleration or deceleration can be seen during that period of time, neither in the velocity gradient plane nor in the vorticity plane. The approaches are smooth and, in terms of the relative velocities, slow. In comparison to the Newtonian case, in the WMS fluid, the particles tend to approach each other somewhat faster, probably due to the shear thinning nature of the fluid. However, no dramatic or unexpected non-linear effects are observed.

Wall and concentration effects

In addition to the effect of normal stress differences, Pasquino and coworkers pointed out that confinement is also a very relevant parameter for promoting alignment, observing an enhancing effect of smaller gap size on structure formation [Pasquino *et al.* (2010b)]. To investigate this effect further, the effect of confinement on both the chain length and the fraction of particles that are part of a string was studied; the results are shown in Fig. 4.

Figure 4(a) shows the fraction of the particles in a string as a function of shear time. Qualitatively, all three curves display a quick increase of the number of aligned particles during the first minutes of the experiment while, afterwards, the growth stagnates and becomes slow. This can be explained by the decreasing collision rate between particles

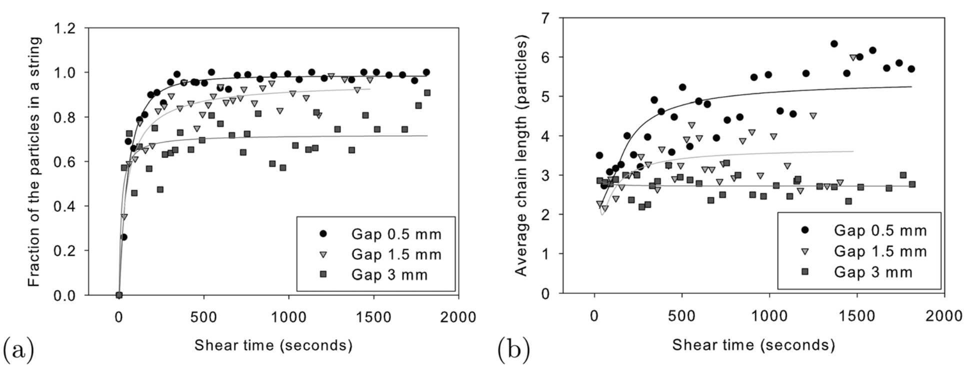

FIG. 4. Effect of confinement on chaining kinetics; (a) chain length, (b) fraction of particles in a string. The system used is the same as in Fig. 2(a); the shear rate is equal to 3.6 s^{-1} in all experiments.

as more spheres are contained in a string. By comparing the three curves in this graph, the effect of confinement can be seen, as for smaller gap heights, more particles are contained in strings. This is also clear from the pseudo steady state values at later times. In Fig. 4(b) the average chain length as a function of shear time is depicted. It can be observed here that the length of the chains increases significantly faster and longer chains are formed at smaller gap heights. Both graphs indicate that confinement is indeed a strongly enhancing factor for string formation by particles in a sheared viscoelastic liquid.

Another aspect of the role of confinement for the formation of strings can be observed in a so-called "cocktail" experiment using the counterrotating setup with the Couette geometry. Here only a layer of the fluid contains particles whereas the liquid layers above and below this layer consist of the suspending medium without particles, as schematically depicted in Fig. 5(a). Although the initial concentration of the suspension layer is the same as in Figs. 2(a), 3, and 4, when shearing this "cocktail," no particle chaining was observed. The absence of string formation can be attributed to an asymmetric interaction distribution that evolves in the vorticity direction, as can be seen in Fig. 5(b). Caused by the absence of confining walls, the particle layer spreads out in time over the height of the cup, probably due to shear induced diffusion. This kind of self-diffusion was observed and explained by Breedveld *et al.* (1998). The developing concentration gradient in the vorticity direction in the particle layer leads to a higher number of interactions of a particle with particles at one side compared to the other side. This asymmetric distribution of interaction leads only to a predominant "kiss-and-tumble" motion without chaining when two particles meet.

These observations, in congruence with 2D simulations results [Choi and Hulsen (2012)], suggest that moderate confinement will increase the tendency of particles to align. A similar effect was observed in the results of Snijkers (2009). Under conditions where string formation was observed in suspensions, two isolated particles were never reported to stay together. However, flow induced particle doublets can be made in the WMS, but at higher shear rate of 4 s^{-1} (not shown here), a shear rate regime not explored in the experiments of Snijkers (2009) and Snijkers *et al.* (2013). So confinement and concentrations effects lower the magnitude of the macroscopic shear rate at which the effects are observed.

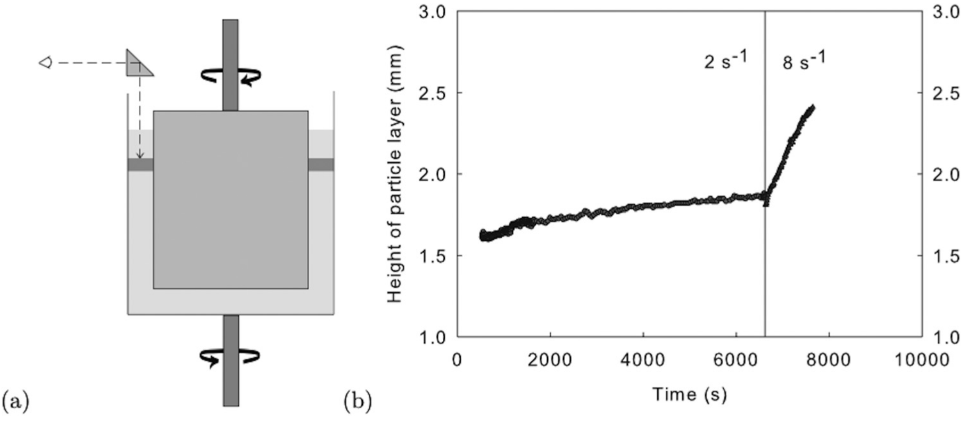

FIG. 5. (a) Cocktail experiment in the Couette cell. The pink layer [height $\mathcal{O}$ (1 mm)] is a CPCl solution containing 0.7 wt. % of 40 μm spheres, and the blue part consists of pure CPCl solution. (b) Height of particle layer as a function of shearing time. The first part was obtained applying a shear rate of 2 s^{-1} (red dots); during the second part of the experiment, the shear rate was increased to 8 s^{-1} (green triangles).

INVESTIGATING HOW PARTICLES SATISFY THE ZERO TORQUE CONDITION

Depletion

While the previous sections mainly focused on how particles approach and form strings, in this section we investigate how the particles act when in a string, either as individual particles or as a collective. Motivated by earlier observations by Pasquino *et al.* (2010b) that the orientation switches from flow aligned to vorticity oriented when attractive interactions become important, we gradually increased the attractive interaction by using a depleting force. We also intend to directly test the mechanism proposed by Santos de Oliveira *et al.* (2012) and evaluate the presence of depletion forces. As depleting agent for the large particles (40 μm PS) smaller particles were used (6 μm PMMA). A suspension of these particles in a wormlike micellar fluid was subjected to shear flow.

When the large spheres come together sufficiently close, their individual rotation is slowed down to a halt and they act as a single body. At low shear rates the particles are observed to stay together for a significant amount of time but still separate eventually, as depicted in Fig. 6(a). Possibly, the orbiting motion of the doublet destroys all possibility for alignment. For the same shear rate and concentration of large particles, but in absence of the small particles, this system shows strong alignment (not shown here). In Fig. 6(b) the shear rate is increased, and elastic forces become important. In this case the dumbbells orient in the vorticity direction similar to ellipsoids [Gunes *et al.* (2008)], for which a drift of the Jeffery orbits towards a log-rolling motion is observed with increasing shear rate. Analysis of the interparticle distance confirms indeed that vorticity-oriented doublets consist of two particles, which are touching or separated by less than 1 μm. Again, also for the rates of Fig. 6(b), in the absence of the small particles, strong alignment is observed. When the shear rate is increased even further, the small particles eventually start to align and form strings. This lowers their effective volume fraction and thus the depletion interaction. The large particles are now free to rotate individually again and form chains. A string of large particles with the small particles aligned in the background can be observed in Fig. 6(c). The particles in flow-oriented strings are separated by several microns, different from the directly touching dumbbells.

By varying the volume fraction, a critical volume fraction of small particles necessary to inhibit alignment of the large spheres can be defined. Using the Asakura and Oosawa (1958), the depletion force for a certain volume fraction can be calculated

$$F = \begin{cases} 0 & h \geq r + R \\ -\dfrac{N}{4V} k_B T \pi (R + r - h)(R + r + h) & h < r + R. \end{cases}$$

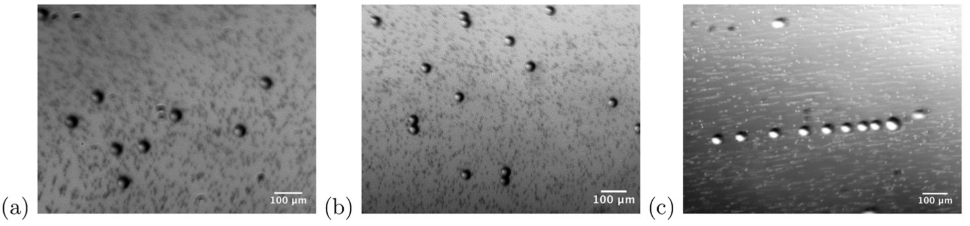

FIG. 6. A wormlike micellar fluid containing 0.35 vol. % 5 μm PMMA particles and 0.35 vol. % 40 μm PS particles. (a) $\dot{\gamma} = 4\ \mathrm{s}^{-1}$, $Wi = 6.5$; (b) $\dot{\gamma} = 6\ \mathrm{s}^{-1}$, $Wi = 11$; (c) $\dot{\gamma} = 10\ \mathrm{s}^{-1}$, $Wi = 19$ (gap of 0.12 mm).

Here F is the attractive depletion force, h is the distance between the surfaces, r is the radius of the small particles, R is the radius of the large particles, $\frac{N}{V}$ is the number density of the small particles, T is the absolute temperature, and k_B is Boltzmann's constant. For the concentrations shown in Fig. 6, this force is small and of the order of 10^{-12} N. At rest no significant attraction is observed, which is in agreement with the non-colloidal nature of the particles. However, during flow, where the depletion effect may be enhanced, the interparticle distance between the large particles is observed to become smaller. The shear stress arising in the gap now slows the rotation of the particles down to the degree where they cannot satisfy the zero toque condition individually anymore but rotate as doublets. Subsequently they act as rigid objects and resemble the dynamics of ellipsoidal particles, which orbit drifting and log-rolling [Gunes *et al.* (2008)].

Rotation of particles in a string

A single sphere suspended in the bulk of a Newtonian liquid under shear flow and in absence of inertia, Brownian motion, or gravitational effects, combined with no-slip boundary conditions at the surface of the particle, displays a rotation speed $\omega = \dot{\gamma}/2$ [Jeffery (1922)]. Snijkers *et al.* (2011) found a slowing down of the rotation in visco-elastic fluids that further decreases with increasing shear rates; they did experiments up to $1\,\mathrm{s}^{-1}$. D'Avino *et al.* (2008) performed simulations for higher shear rates, and their results correspond well to the rotation speed for a single sphere in a WMS measured in the current study. However, literature reports are in disagreement with respect to the rotation rates of individual particles in strings. Michele *et al.* (1977) stated that rotation of the particles vanishes when they are contained in a string, but this was studied only qualitatively. Pasquino *et al.* (2010b) reported a slowing down and a time dependent velocity which was controlled by interparticle spacing. In this study we investigated the rotation behavior by coating a small fraction of the particles partially with gold. The thus obtained Janus particles allow for an easy measurement of the rotation speed. Typical results are shown in Fig. 7. The rotation speed shows only a slight decrease when a doublet is formed. A larger decrease in rotation speed can be observed when the string grows to contain three and four particles. This suggests also that the rotation speed of particles

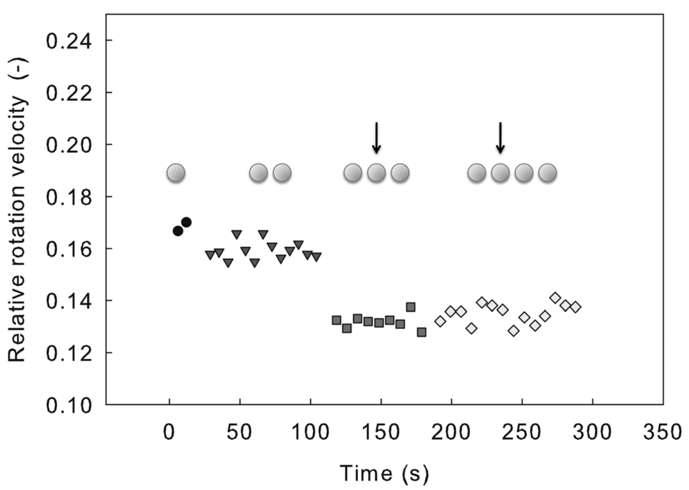

FIG. 7. Rotation speeds of 40 μm polystyrene spheres partly covered with gold. The data were obtained shearing a 0.7 wt. % suspension in a wormlike micellar solution at $3\,\mathrm{s}^{-1}$ ($Wi = 5.4$). The rotation speeds are scaled by the shear rate, a value of 0.5 is expected in the Newtonian case.

within a string of three or more particles should become independent of the string length, which is indeed observed in Fig. 7. This result is also observed in the two dimensional simulations by Hwang and Hulsen (2011) for cylinders.

DISCUSSION

The experimental evidence presented here shows first that a fluid does not need to exhibit any significant normal stress differences to induce alignment, extending the observations already presented by Scirocco *et al*. (2004) from nearly elastic fluids to essentially inelastic fluids. The results suggest that rather than elasticity, shear thinning is a necessary condition for the formation of strings. Compressive effects that are a consequence of the presence of normal forces may speed up the approaching motion and help stabilising strings, as is evidenced from the more pronounced alignment in shear thinning elastic fluids in Fig. 2. Concentration and confinement effects promoting string formation point to a speeding up of the kinetics by increasing the collision probability. Alignment of two isolated spheres in bulk is, however, possible as well, albeit at higher shear rates.

The overall picture suggests that rheological effects become dominant when the particles are close together. The key question seems to be how the particles satisfy the zero torque condition upon approach: as an individual object or not. The effect of even a weak depletion force has clearly shown that the possibility of individual rotation of a particle in a train is crucial for maintaining a stable string in the flow direction.

In a Newtonian fluid, coupling of the pressure and the velocity field causes a divergence of the pressure as the shear rate in the gap increases between approaching particles. The particles are drawn towards each other and act as a rigid body. This causes the particles to tumble, upon which they slowly separate. Shear thinning has a strong effect on lubrication forces and pressures [Lian *et al*. (2001)] and can be expected to weaken the hydrodynamic coupling between two particles. The thin gap between adjoining particles induces locally higher shear rates, which in a shear thinning fluid lead to a low viscosity of the thin fluid layer around a particle. In this case, the effect of velocity on the pressure is somewhat tempered, which helps a fluid layer of a certain thickness to be maintained between the particles. This situation allows each individual particle to satisfy its own zero torque condition, so tumbling does not need to occur.

The local shear rate between two approaching particles can be roughly estimated based on the measured approaching and particle rotation speeds. By dividing the magnitude of the velocity vector for an approaching velocity of 20 μm/s and a rotation speed of 0.2 rad/s by the gap height, shear rates on the order of 1 s^{-1} for a gap of 20 μm to 5 s^{-1} for a gap of 5 μm are obtained. As can be seen from Fig. 1, strong shear thinning sets in from before 1 s^{-1} for the CPCl in water solution and similar values hold for the other fluids used here, confirming the presence of a shear thinning viscosity in the gap upon approach.

STARTUP

To verify this hypothesis on the role of shear thinning, start-up experiments were performed. A sufficiently strong shear flow was utilised to allow two isolated particles to form a stable, flow oriented doublet, or triplet string. Subsequently, the flow was stopped and because the spheres are large and non-Brownian, there is no driving force to break the string apart. This way, a quiescent fluid containing aligned particles is obtained. Subsequently starting up a shear flow creates a different situation. Upon startup, the elastic response is expected to be stronger than the viscous drag [Rehage and Hoffmann (1991)]. In this case, the flow profile in the gap between the particles develops slower than in the fluid surrounding the string, prohibiting thus the development of the lubrication flow and the localised shear thinning. This should inhibit individual particle rotation required to meet the zero-torque condition, which is necessary to maintain the string. The experimental observations are depicted in Fig. 8. For this test, only two particles were used to avoid interference by surrounding particles. Tumbling of the particles in this experiment confirms thus the requirement for the development of shear thinning in the gap when forming strings.

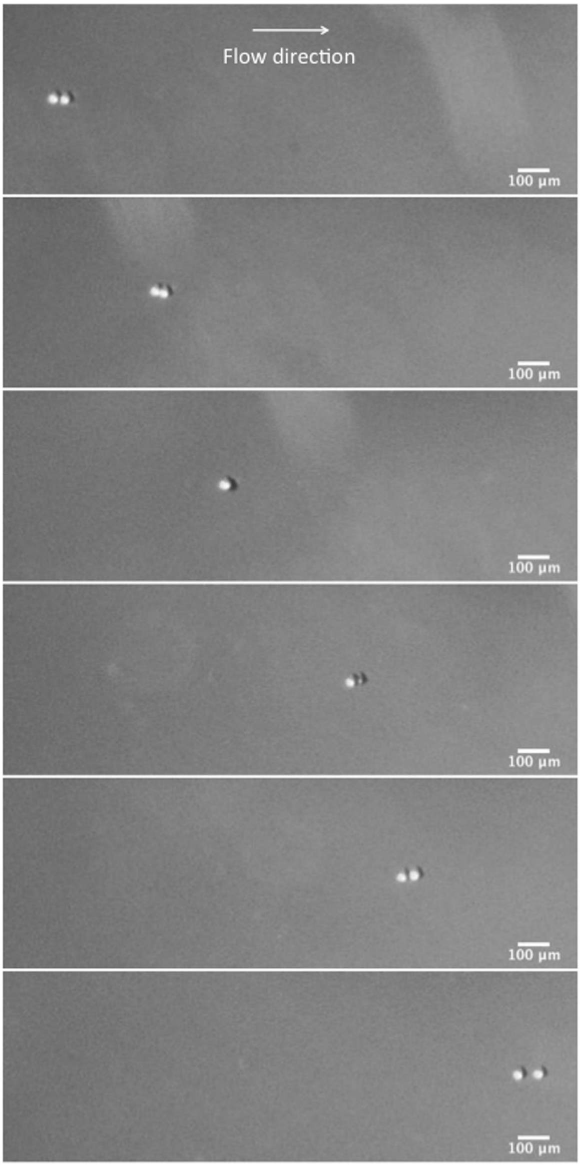

FIG. 8. Tumbling of two particles upon startup: consecutive snapshots when applying shear flow ($6\,s^{-1}$) to a flow-oriented doublet in a WMS. The geometry used here is a parallel plate setup, and the images are made looking through the top plate. The direction of the flow is indicated in the first image.

CONCLUSIONS

In this paper, the role of the rheological properties and a mechanism for particle alignment in sheared viscoelastic fluids was investigated. The proposed mechanism is based on the approaching and collision of particles in shear flow. Normal stress effects can enhance the cross-stream migration and increase the probability of particles encountering each other, but elasticity does not seem to be a necessary condition to make particles meet. Rheological effects of the medium become important only when the particles are already close. Shear thinning allows for the individual rotation of each particle in a string without a diverging lubrication pressure and the subsequent weakened hydrodynamic coupling of the particles prevents particle tumbling. It was shown that flow-induced alignment could be induced for particles suspended in an *fd* virus suspension, which has no measurable normal stresses but does exhibit shear thinning. This shows that the presence of normal stresses is not necessarily required to obtain particles strings. Comparison to fluids with normal stresses, such as the CPCl wormlike micellar solution, does not show that elasticity while not a necessity strongly enhances alignment due to the fact that it creates cross-streamline migration. This was also confirmed by particle tracking experiments, where particles approach faster in a wormlike micellar fluid than in a Newtonian liquid.

Second, in line with earlier observations of Pasquino *et al*. (2010b), experiments with various gap sizes show that confinement leads to faster alignment, probably due to a higher collision probability and the inhibition of shear-induced diffusion. A so-called "cocktail" experiment shows that an uneven distribution of particles is an unfavourable situation for alignment.

Finally, the key question which determines how strings form seems to be how the particles satisfy the zero-torque condition. An elongated body oriented in the flow direction in a shear flow experiences a torque, which would not allow a particle string to exist if it would be a rigid object. Experiments show that, in the range of shear rates explored, particles in a string maintain a certain distance from each other and an individual rotating motion. This is possible in a shear thinning fluid only, where the high fluid velocity in the gap between particles leads to a low viscosity. Pushing the particles together by a depletion interaction forces them to tumble as a whole. Also, a startup experiment, where a particle doublet was shown to tumble, confirms the key role of shear thinning.

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APPENDIX: APPROACHING OF PARTICLES IN A NEWTONIAN SHEAR FLOW

The approaching motion of particles in sheared Newtonian fluid was derived by solving the following set of differential equations, according to the method of Russel *et al*. (1989)

$$U_r = \dot{\gamma}(1 - A)R\sin^2\theta\sin\phi\cos\phi,$$

$$U_\theta = \dot{\gamma}(1-B)R\sin\theta\cos\theta\sin\phi\cos\phi,$$

$$U_\phi = -\dot{\gamma}R\sin\theta\left(\sin^2\phi + \frac{1}{2}B(\cos^2\phi - \sin^2\phi)\right),$$

where

$$U_r = \frac{\partial R}{\partial t},$$

$$U_\theta = R\frac{\partial \theta}{\partial t},$$

$$U_\phi = R\sin\theta\frac{\partial \phi}{\partial t},$$

with $\dot{\gamma}$ the shear rate, θ and ϕ can be seen in Fig. 9, R the distance between the centers of particles, U_r is the derivative of the position of the particle in the direction of line connecting the centers of spheres, U_θ and U_ϕ are similar parameters for the θ and ϕ direction, A and B are defined as follows for spheres of equal size:

$$A = \begin{cases} \dfrac{5}{\left(\dfrac{R}{a}\right)^3} - \dfrac{8}{\left(\dfrac{R}{a}\right)^5} + \ldots & \text{far field solution} \\ 1 - 4.077\dfrac{h}{a} + \ldots & \text{lubrication solution,} \end{cases}$$

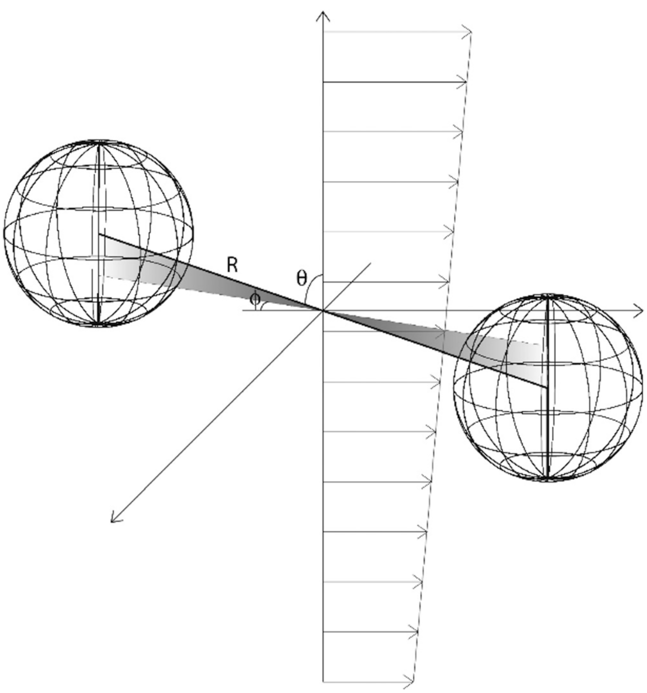

FIG. 9. Schematic representation of two particles in a shear flow.

$$B = \begin{cases} \dfrac{16}{3\left(\dfrac{R}{a}\right)^5} + \ldots & \text{far field solution} \\ 0.4060 - \dfrac{0.78}{\ln\left(\dfrac{a}{h}\right)} + \ldots & \text{lubrication solution,} \end{cases}$$

with a the radius of the particle and h the distance between the surfaces.

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