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Negative normal stress differences N_1-N_2 in a low concentration capillary suspension†

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Abstract

Here, negative normal stress differences are reported in capillary suspensions, *i.e.* particle suspensions in a two-fluid system that creates strong capillary attractions, at a solid concentration of 25%, and a volume fraction that has heretofore been considered too low to show such normal stress differences. Such capillary suspensions have strong particle networks and are shear thinning for the entire range of shear rates studied. Capillary suspensions exist in two states: a pendular state when the secondary fluid preferentially wets the particles, and a capillary state when the bulk fluid is preferentially wetting. In the pendular state, the system undergoes a transition from a positive normal stress difference at high shear rates to a negative stress difference at low shear rates. These results are an indication of flexible flocs in the pendular state that are able to rotate to reorientate in the vorticity direction under shear. Analogous experiments were also conducted for the capillary state, where only a negative normal stress difference occurs. The capillary state system forms more network contacts due to droplet breakup at higher shear rates, which enhances the importance of hydrodynamic interactions in the non-colloidal suspension.

Introduction

The rheological behavior of suspensions can be changed dramatically from a fluid-like state to a gel-like state by adding a small amount of an immiscible secondary fluid to the continuous phase.^{1,2} The attractive capillary force induces a sample-spanning network, which causes a gel-like transition.³ Thus, this kind of system has been termed as a capillary suspension. This phenomenon offers a novel way to tune the flow properties, such as yield stress or aging stability of suspensions, in a simple, inexpensive, and environmentally friendly manner.⁴ Applications of this technique vary from low fat spreadable chocolate^{5,6} to precursors for porous ceramic or glass or polymer membranes,^{7–9} reduction of cracks in

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Conflicts of interest

There are no conflicts to declare.

thin films,¹⁰ printable electronics,¹¹ and stabilization of hydrate slurries for renewable energies,¹² just to name a few.

Depending on the contact angle of the ternary system, we categorize capillary suspensions in two states. If the secondary fluid preferentially wets the particles, the contact angle θ of the system will be smaller than 90° and the system is in the pendular state. If the continuous phase is preferentially wetting, then the contact angle θ of the system will be larger than 90° and the system will be in the capillary state. Bossler and Koos showed a confocal microscopy comparison of both pendular and capillary states.¹³

The strength of the capillary suspension in the pendular state mainly depends on the contact angle and the interfacial tension. While the viscosities of both the secondary fluid and bulk fluid also affect the strength of the capillary suspension, their effect will not be further discussed in this manuscript. As the secondary fluid forms a concave meniscus between the particles, the pressure inside the curvature is lower than the outer meniscus. This negative Laplace pressure difference will cause an attractive potential.¹⁴

An approximation of the capillary force is given by

$$F_c = \frac{2\pi r \Gamma \cos \theta}{1 + 1.05\hat{s} + 2.5\hat{s}^2}, \text{ with } \hat{s} = s\sqrt{\frac{r}{V_1}} \quad (1)$$

where r is the particle radius, s is the separation distance, V_1 is the liquid volume of the secondary fluid, and Γ is the interfacial tension between the liquids.¹⁵ A characteristic property of the capillary suspension is the capillary force hysteresis. As the distance between particles increases, the capillary bridges rupture. Therefore, when the particles approach each other, there is no attractive force until their surfaces come into contact and a capillary bridge is rebuilt.^{14,16}

We use the yield stress to characterize the strength of the gel network, which in our case is caused by attractive capillary forces. By gradually increasing the amount of secondary fluid, the yield stress increases and reaches a plateau regime, as is well known for granular matter and these ternary suspensions.^{17–19} Bossler and Koos showed that typically, a single toroidal bridge connects binary particles, which are in contact ($s = 0$) in the pendular state.¹³ Thus, three spheres in a triangular arrangement are joined by three disconnected toroidal bridges (for a schematic drawing, see the inset of Fig. 1A). As more secondary fluid is added, the filling angle β increases. If a critical β^* is exceeded, the capillary bridges will start to coalesce to form a trimer and other rigid structures.²⁰ The Laplace pressure of the capillary bridge, and therefore, the yield stress of the suspension, is limited by this filling angle.

On a larger length scale, trimers can merge with other dimers or trimers, which will result in larger aggregates, such as pentamers, heptamers, *etc.*²¹ This cluster, with coalesced bridges, is termed as being in the funicular state.^{13,16–18} At a low concentration of secondary fluid, the bridges will predominantly have toroidal shapes, which may lead to anisotropic, lower symmetry clusters. When the bridges start to merge at a higher secondary fluid

concentration, more isotropic, higher symmetry clusters should be formed. These changes in structure would be manifested as differences in the normal stress differences.

Yet, this argument for the pendular state cannot explain percolation in the capillary state. As the contact angle θ is larger than 90° , the meniscus of the liquid is convex, which leads to a positive Laplace pressure and a repulsive force between particles.²² Furthermore, eqn (1) loses its ability to predict the capillary force in the capillary state, since $\cos(\theta > 90^\circ)$ is negative. Koos and Willenbacher proposed that the particles in the capillary state will aggregate around small secondary fluid droplets to minimize energy. They reported that this energy reduction will result in a short-range attractive force. Furthermore, a sample spanning network is formed due to the convection driven collision of the aggregates during the mixing procedure.²³

When a viscoelastic material is sheared between two parallel surfaces, in addition to the shear stress σ_{12} , there can be normal stress differences $N_1 \equiv \sigma_{11} - \sigma_{22}$ and $N_2 \equiv \sigma_{22} - \sigma_{33}$.²⁴ Here, the subscript “1” refers to the shear flow direction, “2” to the axial direction, and “3” to the vorticity direction. These normal stress differences are associated with strain-induced anisotropy.²⁵ For isotropic materials, N_1 is usually zero. In contrast to a normal polymer solution and melt, where N_1 is positive, non-colloidal suspensions show both negative N_1 and N_2 .²⁶ In that case, the magnitude of both N_1 and N_2 is proportional to $\dot{\gamma}$ at low shear rates.

Negative normal stress differences are found for attractive emulsions and suspensions at high concentrations. Montesi *et al.* reported that the onset of a negative N_1 indicates the formation of flocs along the vorticity direction in emulsions near the colloidal glass transition. Their study suggested that the geometry boundary prevents the growth of the flocs in the axial direction (22). They argued that the growth along the shear direction (11) is also restricted, as $\sigma_{11} < \sigma_{22}$. Hence, the flocs can only grow along the vorticity direction (33).²⁷ The stress ratio $|N_1|/\sigma_{12}$ describes the ratio of the elastic force to the viscous force, and it can be used in suspensions to describe the anisotropy. The stress ratio is greater than unity in the later stage of floc formation in the vorticity direction.²⁸

Similar observations of floc formation have been reported for different complex fluids with attractive interactions, such as carbon nanotube suspensions²⁹ and thixotropic clay gels.³⁰ Osuji and Weitz observed that a similar alignment of highly anisotropic flocs in the vorticity direction for a carbon black colloidal suspension also corresponded to the onset of negative N_1 and was an indication of shear thickening.³¹ Negative N_1 as the onset of shear thickening has also been observed in numerical work on dilute colloidal suspensions³² and high concentrated colloidal suspensions.³³ Cwalina and Wagner reported that negative N_1 appears at high shear rates due to the lubrication hydrodynamic contribution. This hydrodynamic stress will increase the possibility of bringing the particles together and squeezing the fluid out of the boundary layer between particles. As a result, these particles will be transiently trapped and form hydroclusters, which is associated with the shear thickening. To the best of our knowledge, there are no systems reported showing negative N_1 for shear thinning at low or intermediate volume concentrations.

In this work, we will demonstrate that negative normal stress differences can exist for a system with an intermediate volume fraction that is shear thinning. We will discuss why the capillary suspension in the pendular state undergoes a sign transition from positive to negative normal stress differences with decreasing shear rates. On the other hand, the capillary state only shows negative normal stress differences. Furthermore, we compare the rheological properties to images obtained from microscopy to gain insight into the network microstructure.

Materials and methods

Materials

Experiments were performed using two different ternary solid–liquid–liquid material systems that consist of spherical micron-sized particles and two immiscible Newtonian fluids. These systems represent the pendular state and the capillary state. An overview of the systems is given in detail in Table 1.

For pendular state samples, we used silica oxide glass (OMicron NP3-P0, Sovitec, Fleurus, Belgium), $d_{50,3} = 3.55 \pm 0.04 \mu\text{m}$, $\rho_{(20^\circ\text{C})} = 2.46 \text{ g ml}^{-1}$ as solid particles and silicone oil (Wacker AK 200 silicone oil, Wacker Chemie AG, Munich, Germany, $\eta = 0.2 \text{ Pa s}$, $\rho_{(20^\circ\text{C})} = 1.07 \text{ g ml}^{-1}$) as the bulk fluid. Glycerol is used as a secondary fluid for the rheological measurements (Rotipuran 99.5%, Carl Roth, Karlsruhe, Germany, $\eta = 1.412 \text{ Pa s}$, $\rho_{(20^\circ\text{C})} = 1.26 \text{ g ml}^{-1}$, $n = 1.474$). For imaging purposes, we substituted the pure glycerol with a mixture of 3 vol% water with PromoFluor dye (PromoFluor-488 premium carboxylic acid, PromoKine, Heidelberg, Germany).

We used cross-linked PMMA beads (Altuglas BS100, Altuglas International, La Garenne-Colombes, France; $d_{50,3} = 22.5 \pm 0.06 \mu\text{m}$, $\rho_{(20^\circ\text{C})} = 1.2 \text{ g ml}^{-1}$, $n = 1.491$) as solid particles for the capillary state. Glycerol is used as a bulk liquid, and paraffin oil as the secondary fluid (Sigma-Aldrich Chemie GmbH, Steinheim, Germany, $\eta = 0.21 \text{ Pa s}$, $\rho_{(20^\circ\text{C})} = 0.88 \text{ g ml}^{-1}$, $n = 1.467$). Nile red was added as a fluorescent dye to the paraffin oil. This dye will not fluoresce in polar liquid. All materials were used as provided by the suppliers.

To confirm that the chosen model system represents the pendular or capillary state, we checked the contact angle of each model system. The contact angle θ of the silica oxide model system was determined using the sessile drop method (OCA 15 EC, Dataphysics, Filderstadt, Germany) and evaluated *via* a numerical Young–Laplace fit to the imaged droplet contour.³⁴ The contact angle of this three phase system was measured to be $\theta = 70 \pm 7^\circ$. For the PMMA–glycerol–paraffin oil model system, we used a custom-build microchannel, as proposed by Bossler and Koos, in combination with confocal microscopy to determine the contact angle.¹³ This system had a ternary contact angle of $\theta = 88 \pm 4^\circ$. The confocal images (Fig. 7) showed that the droplet has a clear convex meniscus, so we can classify this system as in the capillary state. This discrepancy might be caused by the uncertainty during the image analysis. A difference of 1 pixel could cause a contact angle difference of 2° .

Sample preparation

We prepared the pendular state samples using a high-speed disperser (SpeedMixer type DAC 150.1 FVC from Hauschild Engineering, Hamm, Germany), which uses counter-rotation of the 125 ml mixing cups along a central axis (6.7 cm) to increase the homogeneity of the sample. We first mixed silicone oil and glycerol at 1000 rpm for 30 s. The particles are added to the emulsion and the solid–liquid–liquid system is further mixed at 1500 rpm for 180 s. To remove the air bubbles during the mixing procedure, we placed the sample under vacuum (20 mbar) for 25 min.

The capillary state samples were prepared using a different procedure. The PMMA particles were dispersed into the bulk fluid using a dissolver stirrer until a uniform suspension was created (at 2000 rpm for 20 min). We placed the suspension under vacuum (20 mbar for 20 min), then added the secondary fluid to the suspension and mixed using a dissolver stirrer (1000 rpm for 10 min). The capillary suspension was again placed under vacuum (20 mbar for 15 min).

We kept the solid concentration constant ($\phi_{\text{solid}} = 0.25$) for both pendular and capillary state samples. The ratio of secondary fluid concentration to solid concentration was varied between 0.025 $\phi_{2\text{nd}}/\phi_{\text{solid}}$ 0.2.

Rheological measurements

Rheological measurements were carried out using a stress-controlled rheometer Physica MCR 702 from Anton Paar in the separate motor transducer (2EC) mode using the plate–plate geometries LP50 and PP50 with 50 mm diameter. If not specifically stated, the gap height for the measurements was set to 1 mm. All tests were performed at 20 ± 0.5 °C. Two types of sandpapers were used to eliminate wall slip for the pendular state samples: P320 (grit size = $46.2 \mu\text{m}$) for $\phi_{2\text{nd}}/\phi_{\text{solid}} = 0.1$ and P80 (grit size = $201 \mu\text{m}$) for $\phi_{2\text{nd}}/\phi_{\text{solid}} = 0.2$. After filling up the gap with the sample, we waited 2–5 minutes prior to each experiment to make sure that the axial stress due to loading reduced to zero/below the experimental limit. All reported measurements were repeated at least three times with different samples to check their reproducibility. The deviation from the three repetitive tests is shown as error bars.

We chose to use plate–plate geometry for the rheological experiments in our work with the capillary suspensions, so that we can change the measurement gap depending on the particle size. Furthermore, we can ensure that the sample-spanning network due to the attractive capillary force is not destroyed. Thus, due to the inhomogeneous shear rate in the plate–plate geometry, we can only calculate the difference between the first and second normal stress difference

$$N_1 - N_2 = \frac{F_z}{\pi R^2} \left[2 + \frac{d \ln(F_z)}{d \ln(\dot{\gamma}_R)} \right] \quad (2)$$

from the axial thrust F_z and the shear rate at the rim $\dot{\gamma}_R$.³⁵ The effect of the inertia and secondary flows on F_z are eliminated using the correction proposed by Turian³⁶

$$(F_z)_{\text{inertia}} = -0.075\pi\rho\Omega^2 R^4 [1 + 0.004\text{Re}^3] \quad (3)$$

where $\text{Re} = \rho\Omega H^2/\eta$, Ω is the angular velocity, and H is the gap height. The Reynolds number Re for all samples is $\text{Re} \ll 1$, so the second term in the correction is negligible. $(F_z)_{\text{inertia}}$ is the effect of pulling the plate downward and thus its value has to be deducted from the measured normal force before calculating the normal stress differences. Both surface tension and negative Laplace pressure can also cause negative normal force due to the traction contact line or meniscus at the liquid–air interface.^{37–39} This effect should be constant at a given gap and independent of the angular velocity. The approximated contribution of this non-ideal condition is set as the experimental limit. We checked the influence of the surface tension and contact angle on the normal force measurement by running a measurement using hydrophobized sandpaper and no significant influence was found. The normal force measurement limit given by the manufacturer is 1 mN but the experimental limit, calculated from the air–liquid interface, is $|F_z| = 0.03$ N, or $|N_1 - N_2| = 30.6$ Pa.

The normal stress differences $N_1 - N_2$ were investigated for the capillary state samples (PMMA–glycerol–paraffin oil model system) during a flow sweep experiment with increasing shear rates $0.1 < \dot{\gamma} < 500 \text{ s}^{-1}$. The axial force was measured and the difference between the first and second normal stress differences was calculated using eqn (2). The pendular state NP3–silicone oil–glycerol model system is prone to edge fracture during the flow sweep measurement performed with an increasing shear rate, especially at the highest secondary fluid concentration $\phi_{\text{2nd}}/\phi_{\text{solid}} = 0.2$. The edge fracture occurs frequently in flocculated dispersions and shear thickening systems.²⁶ During this flow sweep measurement, we observed irregular curvatures at the sample surface. As the meniscus was present at the free surface, we noticed a non-monotonic trend in the normal force curve (see Fig. S1, ESI†). One assumption for the cause of edge fracture could be heterogeneous network breakup at low shear rates. As can be seen from Fig. S1 (ESI†), the surface instability occurred at stresses at or below the static yield stress, where the cluster size might not be monodispersed. Only the weakest particle–secondary fluid bonds would break at the applied low shear rates. However, this topic has to be studied thoroughly later to understand the underlying physics of edge fracture in capillary suspensions. Edge fracture is problematic when measuring normal stress differences because it affects the normal stress distribution throughout the sample, and should be avoided.

Therefore, we decided to execute the flow sweep experiment with decreasing shear rates for the NP3–silicone oil–glycerol samples. Using decreasing rates, we observed no evidence of edge fracture and we were able to systematically investigate the restructuring of the network. A pre-shear with $\dot{\gamma} = 10 \text{ s}^{-1}$ for 15 seconds was used to erase possible cluster orientation during the loading step for the NP3–silicone oil–glycerol samples, after which we conducted a flow sweep for $100 > \dot{\gamma} > 0.1 \text{ s}^{-1}$. The underlying physics as to why decreasing shear rates could suppress edge fracture is not yet known. The highest shear rate ($\dot{\gamma} = 100 \text{ s}^{-1}$) was sufficient to break up the sample-spanning network and should set a statistically equivalent

initial starting point for network restructuring. The differences in the flow curve and normal force between the flow sweep measurements with increasing and decreasing shear rates are shown in Fig. S2 (ESI†) and between samples for decreasing shear rates in Fig. S3 (ESI†). The Herschel–Bulkley model was used to obtain the dynamic yield stress from the flow sweep during network restructuring. For the PMMA–glycerol–paraffin oil model system, a pre-shear was not required.

Static yield stress measurements were carried out by stepwise linearly increasing the shear stress (0.1 Pa s^{-1}) in the range from $\sigma = 0.1$ – 1000 Pa , with a maximum shear rate of $\dot{\gamma}_{\text{max}} = 200 \text{ s}^{-1}$ as a measurement stopping criterion. The logarithmic deformation is plotted as a function of the logarithmic shear stress and the intersection of the two tangents is used to determine the static yield stress σ_y . Capillary suspensions have the ability to rebuild their networks upon cessation of high shear rates. To study this phenomenon systematically in the capillary state, we compared the static yield stress measurement after the sample preparation and after being sheared with high shear rates using a capillary rheometer. If not specifically stated, we use the term yield stress for the static yield stress.

Microscopy imaging

We used a Leica TCS SP8 inverted confocal laser scanning microscope (Leica Microsystems, Mannheim, Germany) to take the confocal and bright field microscopy images. For the PMMA–glycerol–paraffin oil model system, the paraffin oil (secondary fluid) was dyed with Nile red. The dye was excited by a 552 nm laser and the signal, emitted in a wavelength interval of 560–660 nm, was recorded. The particles and aqueous glycerol (bulk fluid) were undyed.

To visualize the NP3–silicone oil–glycerol model system after shearing with specific, low shear rates using a shear cell RheOptiCAD system obtained from CAD Instruments, we overlay the bright field and the confocal mode of Leica TCS SP8.40 The PromoFluor dye in the aqueous glycerol (3 vol% water) was excited by a 488 nm laser and emission was recorded between 448 and 555 nm. The samples were placed between two parallel cover glasses, and the gap was set to 1000 and 250 μm . We stopped the measurement after a steady state was achieved, and captured the images.

Results and discussion

Pendular state

In the NP3–silicone oil–glycerol model system for the pendular state, we determined both the static and dynamic yield stresses, and compared the results, as displayed in Fig. 1A. In the figure, the solid concentration is kept constant at $\phi_{\text{solid}} = 0.25$ while the amount of secondary fluid added is varied between $\phi_{2\text{nd}}/\phi_{\text{solid}} = 0.025$ and 0.2. The normal suspension also showed a yield stress, which indicates network formation due to van der Waals forces. The increase in yield stress due to the addition of secondary fluid is caused by the capillary force.

The increase in static and dynamic yield stresses for $\phi_{2\text{nd}}/\phi_{\text{solid}} = 0.025$ and 0.05 indicates an increasing number of particles connected by toroidal capillary bridges. Upon the addition of

secondary fluid, exceeding the critical filling angle β^* , the capillary bridges collapse. As a result, a more compact, isotropic cluster is formed. These transitions are sketched in Fig. 1B. Since the Laplace pressure is a function of the filling angle β and the contact angle θ , an unvarying β will result in constant Laplace pressure and constant yield stress. This plateau in the yield stress indicates a transition from the pendular to funicular state.^{9,13,19,20} Beyond this secondary fluid concentration, the particles will be immersed in the secondary fluid and the capillary bridges no longer exist, causing a reduction in the static yield stress. The microscopic images (Fig. 2) show that clusters in the samples with $\phi_{2nd}/\phi_{solid} = 0.05$ look more like chains, while clusters in the sample with $\phi_{2nd}/\phi_{solid} = 0.2$ are more compact, but still isotropic.

As mentioned in the Materials and methods section, the pendular state samples suffer from an edge fracture during flow sweeps with increasing shear rates. Therefore, we ran flow sweeps with decreasing shear rates, where we did not observe such an instability. Furthermore, this procedure enabled us to investigate the network rebuilding process for capillary suspensions, which we consider as thixotropic samples.⁴¹ As shown in eqn (1), there is a hysteresis in the capillary force and it depends on the distance between the connected particles. This is similar to other thixotropic materials with attractive interactions. Their rheological properties depend on the balance between the attractive forces and the shear forces as well as their shear history. Thixotropic materials rebuild their structures upon a reduction or cessation of shear.⁴²

The normal suspension and pendular state samples show shear thinning behavior, as indicated in Fig. 3A. The capillary suspension samples have higher viscosity compared to the normal suspension, since the capillary force is stronger than the van der Waals force. The inset graph shows that the viscosity as a function of secondary fluid concentration at a shear rate of $\dot{\gamma} = 1 \text{ s}^{-1}$ reaches the maximum at $\phi_{2nd}/\phi_{solid} = 0.05$. Compared with the dynamic yield stress (Fig. 1A), the viscosities of the funicular state samples are lower than for the pendular state, but the effect is less pronounced for the viscosity data. At higher secondary fluid concentrations, the flocs are more compact and isotropic, thus they have less influence on the viscosity. At high shear rates, the curves almost coincide, with $\eta(\dot{\gamma}=100 \text{ s}^{-1}) = 1.3 \text{ Pa s}$ for the normal suspension and $\eta(\dot{\gamma}=100 \text{ s}^{-1}) = 1.9\text{--}2.3 \text{ Pa s}$ for the capillary suspensions with different ϕ_{2nd}/ϕ_{solid} . This difference indicates that some clusters are still present at the highest shear rates used, leading to a higher effective volume fraction ($\phi_{solid,eff} = 0.4$ for the normal suspension and $\phi_{solid,eff} = 0.45\text{--}0.48$ for the capillary suspensions, according to the scaling of Sierou and Brady⁴³). The effective volume fraction of the capillary suspensions suggests a larger hydrodynamic radius where two or three particles come together.

As shown in Fig. 3B, the normal stress differences of the NP3–silicone oil normal suspension are slightly negative but fall within the experimental limit. Interestingly, on the other hand, the capillary suspensions undergo a transition from positive normal stress differences at high shear rates to negative differences at low shear rates. The influence of inertia correction ($(F_z)_{inertia} \sim \Omega^2$) on the pendular state is small. At the highest shear rate ($\dot{\gamma} = 100 \text{ s}^{-1}$), the inertia correction results in a difference of 7.2–10.5% in the normal stress differences for the different concentration of secondary fluid, which falls within the error bars. The trend in the magnitude of the negative normal stress differences at low shear rates

is consistent with the result obtained from the dynamic yield stress and the low shear viscosity. The capillary suspension with $\phi_{2nd}/\phi_{solid} = 0.05$ has the highest magnitude of normal stress difference that drops with a higher ratio of ϕ_{2nd}/ϕ_{solid} .

Two processes occur simultaneously during shearing: stochastically driven cluster formation as soon as particles and droplets of secondary fluid come into contact, and cluster break-up due to the viscous force. A transition from spherical particles to non-spherical dimers occurs when these clusters are formed. Under shear, the motion of these dimers and other asymmetric clusters follows a Jeffery orbit for rigid particles, which describes the ‘kayaking’ motion around the vorticity axis.⁴⁴ The two extremes for Jeffery orbits are rotation around the symmetric axis (or alignment in the vorticity direction) and rotation in the flow-velocity gradient plane. Long, slender particles and clusters tend to stay longer in the vorticity direction, while particles with more rigid shapes like disks tumble in the flow-velocity gradient plane. In the absence of Brownian motion, the orbit depends solely on the hydrodynamic interaction and its period is inversely proportional to the shear rate.²⁶

The influence of tumbling in the flow-gradient plane dominates at high shear rates since the hydrodynamic force is dominant. During the tumbling, friction occurs as these clusters come into contact due to the attractive capillary force. As a result, all capillary suspensions show positive normal stress differences, which is consistent with the results of Petrich *et al.* for friction during fiber contacts.⁴⁵ The effective, hydrodynamic diameter of the cluster at high shear rates ($\dot{\gamma} = 100 \text{ s}^{-1}$), calculated from rheology by assuming isotropic clusters, was two or three times larger than the particle size. If, instead, we assume that the clusters consist of chained particles, they can be modeled as cylinder or slender spheroids with an unknown aspect ratio. Using the theory of Shaqfeh and collaborators for non-Brownian, slender spheroids with random orientation, an aspect ratio of 3.3 can be predicted.^{46,47}

The flocs grow as the shear rate decreases. The relative difference between each concentration of secondary fluid is more pronounced, which is related to the structure of the formed network. The onset of negative normal stress differences indicates that the clusters start to orientate in the vorticity direction. Since the magnitude of the negative normal stress differences for the samples with low ratios of $\phi_{2nd}/\phi_{solid} = 0.025$ and 0.05 are similar (see Fig. 3B), as are the samples with ratios of $\phi_{2nd}/\phi_{solid} = 0.1$ and 0.2 , we will only use the samples with the ratios of $\phi_{2nd}/\phi_{solid} = 0.05$ (pendular) and 0.2 (funicular) to simplify the further discussion. Fig. 4 shows the microscopic images of both samples prior to shearing, at rest and after being sheared with different shear rates ($\dot{\gamma} = 1, 0.5, 0.1 \text{ s}^{-1}$) at which negative normal stress differences emerge.

Prior to shearing, the clusters appear to be evenly distributed. During shearing, the flocs break-up and reform into new clusters. The sample with $\phi_{2nd}/\phi_{solid} = 0.05$ has predominantly linear, flexible flocs. Due to the fixed gap height, they are not able to grow in the shear gradient direction.²⁷ The flocs also cannot grow in the shear direction since there will always be competition between capillary bridge destruction and reformation. This leads to solid-body reorientation into the vorticity direction and, hence, negative normal stress differences are measured.

With increasing concentration of the secondary fluid ($\phi_{2nd}/\phi_{solid} = 0.2$), the flocs become more isotropic and exhibit rigid body motion. A mixture of anisotropic clusters, particle-stabilized droplets, and polytetrahedral clusters was also observed in the sample. The compact clusters and particle-stabilized droplets were stable against low shear rates, whereas the anisotropic flocs reorientated in the vorticity direction. Since the fraction of the anisotropic flocs was limited, the sample exhibited a lower magnitude of normal stress differences.

To understand the influence of the gap variation on the rheological properties, we repeated the flow sweep measurements with a smaller gap of 250 μm (from 1 mm). As can be seen from the viscosity curve inset in Fig. 5A, the apparent viscosities of the pendular state sample ($\phi_{2nd}/\phi_{solid} = 0.05$) for the two different gap heights at $\dot{\gamma} = 1 \text{ s}^{-1}$ are nearly identical, while the funicular state sample ($\phi_{2nd}/\phi_{solid} = 0.2$) shows a higher apparent viscosity at a smaller gap. At $\dot{\gamma} = 100 \text{ s}^{-1}$, the viscosity difference between the two different gaps is negligible for both samples, which supports the conclusion that the hydrodynamic force dominates at the high shear rate.

The funicular sample shows positive normal stress differences at high shear rates, where the magnitude is nearly independent of the gap height, as shown in Fig. 5B. In contrast, the pendular state sample ($\phi_{2nd}/\phi_{solid} = 0.05$) at the smaller gap shows a plateau in the negative normal stress differences, where the values are close to the experimental limit. This implies that the structure of the funicular state sample at high shear rates is not greatly affected by the gap reduction whereas it is affected in the pendular state. The inertia correction for $\phi_{2nd}/\phi_{solid} = 0.05$ at the smaller gap for $\dot{\gamma} = 100 \text{ s}^{-1}$ results in a 30% reduction in the magnitude of negative normal stress differences, leading the results being situated closer to the experimental limit. However, this result confirms that the negative normal stress differences are not an inertia effect as the correction for $\phi_{2nd}/\phi_{solid} = 0.2$ has negligible influence on the normal stress differences ($<1\%$). For low shear rates ($\dot{\gamma} \sim 10 \text{ s}^{-1}$), both samples exhibit similar negative normal stress differences at the smaller gap. Yet, their magnitude is higher compared to the magnitude at the larger gap, which confirms the results of Montesi *et al.* for vorticity aligned flocs at various gap heights.²⁷

Furthermore, Fig. 5 shows excellent reproducibility and low error in viscosity measurements, while the normal stress differences are more prone to deviation. To show the measurement reproducibility, we plot an example of these tests with three repetitive measurements on different loadings in Fig. S3 (ESI[†]) without data averaging.

Fig. 6 reveals the microstructures of the sample after being sheared at $\dot{\gamma} = 0.5 \text{ s}^{-1}$ for the two different gap heights. For the sample with $\phi_{2nd}/\phi_{solid} = 0.05$, a smaller gap caused the local concentration of the particles to increase, presumably because the oil-phase is expelled from the sample. The gap reduction also intensifies the growth restriction in the shear gradient direction, further extending the clusters in the vorticity direction. As a consequence, the magnitude of negative normal stress differences increases (Fig. 5B). This confinement induced structure might also explain why this sample shows negative normal stress differences at high shear rates.

However, the higher magnitude of the negative normal stress differences in the funicular state sample may not be caused by vorticity alignment. As mentioned previously, the size of the flocs can grow as the shear rates decreases. Funicular clusters under shear can easily merge to form polytetrahedral aggregates with large numbers of particles connected by a single, continuous droplet. As the gap decreases, the continuum assumption may no longer be valid. Fig. 6 shows that the funicular sample has a broad distribution of cluster sizes at the smaller gap. The size of the large funicular clusters is approximately one third of the gap size. Since the funicular clusters are more isotropic and rigid, stochastic collisions under shear can cause them to span between the two walls and form a force chain. This force is dominated by the short range attractive capillary force. As a result, the viscosity and the magnitude of the negative normal stress difference will both increase. Such an increase in viscosity under extreme confinement (gap size smaller than three particle diameters) has been reported in the literature for a monodisperse sample with high particle concentration ($\phi = 0.52$) and at moderate volume fractions ($\phi = 0.05$ – 0.3).^{48,49}

Capillary state

The PMMA–glycerol–paraffin oil model system for the capillary state showed an enhanced yield stress for increasing ratios of ϕ_{2nd}/ϕ_{solid} , as indicated in Fig. 7A. The solid fraction was kept constant ($\phi_{PMMA} = 0.25$). The corresponding confocal microscopy images give insight into the microstructure of the capillary state sample with various amounts of added secondary fluid. The volume size of the droplets increases in proportion to ϕ_{2nd}/ϕ_{solid} . They confirm the simulation results of Koos and Willenbacher that the microstructure undergoes a transition from flocs with some free particles to tetrahedral and then polytetrahedral structures with increasing concentration of the secondary fluid (see Fig. 7A).²³ As reported above, the surface energy reduction is proportional to the increasing number of building blocks, which is then reflected in the increase of yield stress.

Compared to the Newtonian PMMA–glycerol suspension, $\phi_{2nd}/\phi_{solid} = 0$, the capillary suspensions show increasing viscosities at low shear rates. The magnitude of the viscosity increase is proportional to the amount of secondary fluid. Each capillary suspension curve exhibits shear thinning behavior. The viscosities of all samples are identical to that of the pure PMMA–glycerol suspension at high shear rates (Fig. 8A). This indicates that the viscous force dominates over the elastic capillary force and the capillary bridging mechanism is not present at these high shear rates.

Just like the glass–silicone oil suspension for the pendular state, the normal stress differences in the PMMA–glycerol suspension are zero, therefore typical Newtonian behavior is expected for this normal suspension (Fig. 8B). This result does not match with those of Zarraga *et al.*, where they reported that N_1 – N_2 for non-Brownian suspensions are always positive and have a scaling of N_1 – $N_2 \sim \sigma \phi^3 e^{2.34\phi}$.⁵⁰ They showed that both N_1 and N_2 are negative with $|N_1| < |N_2|$. Using a linear regression in ϕ , our normal suspension ($\phi_{2nd}/\phi_{solid} = 0$) is expected to scale with N_1 – $N_2 = 0.03\sigma$. This discrepancy can only be explained by considering their particle sedimentation ($\rho \sim 1000 \text{ kg m}^{-3}$) in normal stress calculations. The buoyancy is negligible for our PMMA–glycerol suspension ($\rho = 60 \text{ kg m}^{-3}$). Furthermore, this correlation was only predicted to fit the data range of $\phi = 0.3$ – 0.5 ,

which is higher than our solid concentration ($\phi_{\text{solid}} = 0.25$). Our results, however, do match the simulation data of Sierou and Brady, where $N_1 \approx N_2$ in the absence of interparticle forces, leading to negligible $N_1 - N_2$ for $\phi_{\text{2nd}}/\phi_{\text{solid}} = 0.43$. Additionally, our data are consistent with the experimental results of Singh and Nott, where the normal stress differences in neutrally buoyant non-Brownian suspensions for $\phi_{\text{solid}} < 0.30$ were too small to be accurately measured.⁵¹

In contrast, each capillary state suspension shows purely negative normal stress differences. Their magnitude increases at high shear rates with the exception of the normal stress difference for the sample with $\phi_{\text{2nd}}/\phi_{\text{solid}} = 0.2$, which is within the experimental limit. The reported values here are the normal stress differences after the raw data had undergone inertia correction, which results in a 23–39% reduction in magnitude of the negative normal stress differences at $\dot{\gamma} = 100 \text{ s}^{-1}$ compared to the uncorrected values. A comparison of the normal forces for all samples in the capillary state before and after the inertia correction is shown in Fig. S4 (ESI[†]). The increase of the magnitude of negative normal stress differences at high shear rates could indicate a change in the microstructures caused by the hydrodynamic force. Since the increase of the magnitude of negative normal stress differences occurs only for the last two data points, we decided to prove this hypothesis by shearing the capillary state suspensions at even higher shear rates using a capillary rheometer (Rheograph 6000 from Göttfert, Buchen, Germany). The capillary rheometer is only used to force the capillary suspension through a nozzle at certain, well-defined shear rates.

The capillary state suspensions were subjected to a specific, variable shear rate in the capillary rheometer where we only collected the sample after a steady state was achieved. Shortly after each high shear rate sample was prepared, we performed confocal microscopy imaging and yield stress measurements to prevent a pronounced aging effect on the samples. As seen in Fig. 9A, the size of droplets decreases and the number of droplets increases with increasing capillary rheometer (mixing) shear rates. The greater number of available droplets serve as the basic building blocks for the capillary state network with the strongest network occurring with the tetrahedral building blocks.²³ Thus, at high mixing rates, longer unidimensional clusters with lower symmetry will be shaped, which are better suited to forming a sample-spanning network.⁵² This is demonstrated in the increase in yield stress in Fig. 9B up to $\dot{\gamma}_{\text{mixing}} \sim 3000 \text{ s}^{-1}$. However, once a critical droplet size is exceeded, the particles will not be able to shield the droplet anymore and a tetrahedral cluster is no longer possible. These droplets can stay at the surface of the particles without contributing to network formation. This is manifested in the decrease of yield stress.

At high shear rates, the viscous force will cause a competition between separations of the particles and the droplets and convection driven collisions. The network restructuring in the capillary state occurs in several steps. First, the high shear rates detach the secondary fluid droplets. Second, the high shear deformation causes new droplet break-up. Droplet break-up in concentrated dispersions occurs at lower shear rates than in dilute ones.^{53–55} The critical shear rates for new droplet breakup can be approximated using a modified mean-field model, based on concentrated emulsions, where the influence of the particles on the droplet break-up is also incorporated.⁵⁴

$$Ca_{crit}^* = \frac{\eta_{bulk+solid} \cdot \dot{\gamma}_{crit} \cdot R_{droplet}}{\Gamma_{bulk,droplet}}, \text{ and } \lambda^* = \frac{\eta_{droplet}}{\eta_{bulk+solid}} \quad (4)$$

where the capillary number Ca^* is the ratio of the viscous force to the surface tension between two immiscible liquids. In our model system, the viscosity ratio $\lambda^* = 0.06$ yields a critical capillary number $Ca_{crit}^* = 0.5\text{--}0.6$, or $\dot{\gamma}_{crit} = 530\text{--}640 \text{ s}^{-1}$ for the capillary state suspensions. The viscosities of both liquids are significant for the droplet break-up and later the network rebuild, as their ratio influences the capillary number. However, since we fixed the choices of the immiscible liquids for all capillary state samples, we will not further discuss the influence of the liquid viscosities.

Kaur and Leal showed that droplet and particle will collide under shear. The size of the particles in comparison to the droplets is important for the droplet break-up, where they observed no significant droplet deformation if the particles are much smaller than the droplets.⁵³ The presence of particles leads to local deformation of the droplet interface, which causes droplet breakup as the distance between droplet and particle decreases.⁵⁶ This occurs at lower shear rates compared to the predicted critical shear rate for a dilute system or emulsion. This explains why we also observed an increase in the yield stress for the samples that were sheared at $\dot{\gamma} = 190 \text{ s}^{-1}$ in Fig. 8B. Indeed, such a yield stress might be caused by the droplet break-up and this might begin to occur at $\dot{\gamma} \approx 100 \text{ s}^{-1}$ where there is a change in the normal stress differences (Fig. 8B). Due to the geometry boundary, these clusters can only grow in the vorticity direction, which is represented by the onset of the magnitude increase of negative normal stress differences. However, the normal stress differences are difficult to capture at these high shear rates, since their values are at the limit of our measurement resolution. A new experiment must be designed to report network restructuring at high shear rates.

Conclusions

In this article, we demonstrated negative normal stress differences on capillary suspensions at low particle volume fraction ($\phi_{solid} = 0.25$) and with variation of the ratio of secondary fluid concentration to the solid fraction ($0.025 \leq \phi_{2nd}/\phi_{solid} \leq 0.2$) in both the pendular state and capillary state. In confirmation with the literature, negative normal stress differences appear in a system with attractive interaction, the capillary force in this case. However, such negative normal stress differences have not been reported before for samples at low volume fraction and with shear thinning behavior as shown here. Furthermore, we demonstrated that the change in the normal stress was an important indication of network restructuring.

We investigated the network rebuilding mechanism of the pendular state samples by decreasing the shear rates. The NP3–silicone oil–glycerol model system undergoes a transition from positive normal stress differences at high shear rates to negative stress differences at low shear rates. The positive normal stress differences at high shear rates indicate the dominance of the viscous hydrodynamic force over the elastic capillary force. The small clusters tumble in the flow–flow gradient plane, following a Jeffery orbit. During

the tumbling, friction occurs as clusters come into contact, due to the attractive capillary force. As the floc break-up and rebuild occur simultaneously under shear, the clusters grow as the viscous force is decreased. The onset of negative normal stress differences implies some of the cluster domains extend in the vorticity direction, as confirmed by the confocal microscopy images.

Under confinement, the magnitude of the negative normal stress differences at low shear rates is more pronounced. For the lower secondary fluid concentration, which has more anisotropic, flexible clusters, a smaller gap causes a more extreme restriction in the growth of the clusters in the shear gradient direction. Consequently, these anisotropic clusters align predominantly in the vorticity direction. However, the flocs are more rigid and isotropic at the higher concentration of secondary fluid. The rigid, polytetrahedral clusters grow, as they collide under shear. The clusters can form force chains, which increase the viscosity at low shear rates and this increases the magnitude of negative normal stress differences at the smaller gap of 250 μm compared to 1000 μm . However, the continuum mechanics assumptions may not hold anymore under extreme confinement due to the large size of these clusters.

In the capillary state, the PMMA–glycerol–paraffin oil model system only shows negative normal stress differences with a magnitude that increases at the high shear rates. The onset of the increase of negative normal stress differences indicates network restructuring, as the high shear rates detach the kinetically trapped secondary fluid droplets. The free droplets deform and break-up under high shear rates, leading to a smaller droplet size, as confirmed by the confocal images. The viscosities of the immiscible fluids also influence the droplet break-up. Due to stochastically driven convection between the particles and the smaller droplets, droplet shielding occurs, leading to a surface energy reduction and the attractive capillary force. As these clusters grow, they are no longer able to grow in the shear gradient direction because of the solid boundary. As a result, they reorientate in the vorticity direction, which is manifested in the increasing magnitude of negative normal stress differences.

While we only investigated this phenomenon using two different model systems, the normal stress differences in capillary suspensions should be further exploited with different material combinations. This research offers a clear pathway to fine tune the form and the direction of the pores in capillary suspension-based porous materials, such as membranes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

(A) Yield stress curve of the pendular state samples (NP3–silicone oil–glycerol) with various ϕ_{2nd}/ϕ_{solid} where the circle refers to the static yield stress and the square is the dynamic yield stress, calculated with the Herschel–Bulkley fit. The inset shows a schematic diagram of the correlation between the volume of capillary bridges and the filling angle β (after Scheel *et al.*20). (B) Corresponding schematic diagrams showing the microstructure. Different frames are used to divide these samples into the three proposed regions.

Fig. 2.

Overlay of confocal fluorescence and bright field images for various ϕ_{2nd}/ϕ_{solid} at the quiescence. Different frames are used to divide these samples into three proposed regions, as shown in Fig. 1B. The lower images show the higher magnification of the clusters in the pendular state ($\phi_{2nd}/\phi_{solid} = 0.05$) and the clusters in the funicular state ($\phi_{2nd}/\phi_{solid} = 0.2$) with their corresponding schematic diagrams.

Fig. 3.

Viscosity (A) and normal stress difference curve (B) of pendular state as a function of the ratio of secondary fluid concentration to solid concentration ϕ_{2nd}/ϕ_{solid} . Gap was set to 1 mm. Flow sweep measurement was executed with decreasing shear rate. The inset shows the viscosity as a function of concentration of the secondary fluid at shear rate $\dot{\gamma} = 1$ s⁻¹.

Fig. 4.

Overlay of confocal fluorescence images and bright field images obtained from the sample with $\phi_{2nd}/\phi_{solid} = 0.05$ (top) and 0.2 (bottom) after being sheared with different shear rates. Images on the left show the sample at the quiescent state where the clusters are homogeneously distributed. The dashed lines are the guide to the eyes, to show examples of the flocs. The lines were drawn after the images had undergone some post-processing operations, which included grayscale conversion, smoothing, Gaussian blur and edge detection. These lines are extracted as a new layer and then overlayed on the confocal-bright field images. The dashed lines (— —) on the upper images show the examples of linear, flexible flocs and the dash-dot-dot lines (— · · —) on the lower images show the examples of mixtures of particle-stabilized droplets and more compact flocs. The gap was 1 mm and the scale bar is the same for all images.

Fig. 5.

(A) Viscosity and (B) normal stress differences for the pendular and funicular states as a function of shear rates for two different gap heights and the secondary fluid concentrations $\phi_{2\text{nd}}/\phi_{\text{solid}} = 0.05$ (squares) and 0.2 (circles). Filled symbols represent 1 mm gap and empty symbols represent a gap of 250 μm . The inset curves magnify the viscosities as a function of secondary fluid concentrations at $\dot{\gamma} = 1 \text{ s}^{-1}$ and $\dot{\gamma} = 100 \text{ s}^{-1}$. The measurements were executed with a decreasing shear rate, as indicated by the arrow.

Fig. 6. Overlay of confocal fluorescence and bright field images obtained from the sample with $\phi_{2nd}/\phi_{solid} = 0.05$ (top) and 0.2 (bottom) after being sheared with $\dot{\gamma} = 0.5 \text{ s}^{-1}$. The gap was 1 mm (left) and 250 μm (right).

Fig. 7.

(A) Yield stress at various ratios of secondary fluid to the solid fraction. The line is to guide the eyes. (B) Corresponding confocal microscope images with (I) $\phi_{2nd}/\phi_{solid} = 0.05$, (II) $\phi_{2nd}/\phi_{solid} = 0.1$, (III) $\phi_{2nd}/\phi_{solid} = 0.2$. The upper images show a 2D-image slice and the lower images are the image of the 3D stack. Paraffin oil, the secondary fluid, is dyed with Nile red and appeared as red droplets. The intensity of the images is enhanced, so the PMMA particles ($\phi_{solid} = 0.25$) are more visible (shown as a red ring. See the example particles, denoted by arrows, in each image).

Fig. 8.

Viscosity curve (A) and normal stress differences (B) for the capillary state suspension with various amounts of added secondary fluid ϕ_{2nd}/ϕ_{solid} .

Fig. 9.

(A) 2D-confocal microscopy images of the capillary state samples after being sheared in a capillary rheometer with various shear rates. (B) Corresponding yield stress curve for various secondary fluid concentrations. The dashed lines denote the yield stress of the samples after sample preparation ((dashed line --) for $\phi_{2nd}/\phi_{solid} = 0.05$, (dash-dot line -.-) for $\phi_{2nd}/\phi_{solid} = 0.1$, and (short-dot line ···) for $\phi_{2nd}/\phi_{solid} = 0.2$), as shown in Fig. 7 (left), and prior to the mixing step.

Table 1

Overview of the materials used for the capillary suspensions

State	Solid	Bulk fluid	Secondary fluid
Pendular	Silica oxide glass	Silicone oil	Glycerol
Capillary	PMMA beads	Glycerol	Paraffin oil