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Report:

The changes induced by flow of the non-equilibrium structure in weakly aggregated suspensions were investigated. Model suspensions consisting of organophilic spherical silica particles with an average diameter of 26.8 nm (with 12% polydispersity) dispersed in an organic solvent were used. They are organophilic due to a grafted layer of 1-octadecanol on their surface. The particles were dispersed in n-tetradecane at volume fractions ranging from 0.05 to 0.3. At elevated temperatures (above 50 °C) these suspensions are stable, upon cooling of the suspension a critical temperature is reached at which they form a sticky sphere dispersion which gels at sufficient high volume fraction. Due to the thermoreversibility, mechanical history effects could be wiped out by a thermal protocol. The suspensions were subjected to shear flow by using a polycarbonate Couette flow cell. Experiments were conducted using either a 2D SAXS detector or a 1D USAXS detector to obtain information on a wide range of lengthscales.

(Quiescent) structure from USAXS measurements.

Figure 1a displays the quiescent scattering pattern of a 5% dispersion at different temperatures. For reference the scattering cure at an elevated temperture of 60 °C is also shown. From the slope of the scattering curve a fractal dimension of 2.4 is obtained, which is in good agreement with values observed for other sticky sphere suspensions [1,2]. Hence at rest a fractal network develops. The quiescent structure in the gel state is quite temperature independent as can be inferred from figure 1a. In modelling attemps of the flow behaviour of reversible aggregated suspensions the flocs are assumed to be fractal [3] even during flow. Strong changes in the floc size are held responsible for the non linear rheological properties. USAXS measurements were also used to monitor the floc size during flow. A weak dependance on shear rate was observed (see figure 1b and inset). It has been suggested that

the fractal concept does not apply during flow, as light scattering experiments of sticky sphere dispersions in shear flow are at odds with this assumption because they show a profound ansiotropy in the scattering pattern [1].

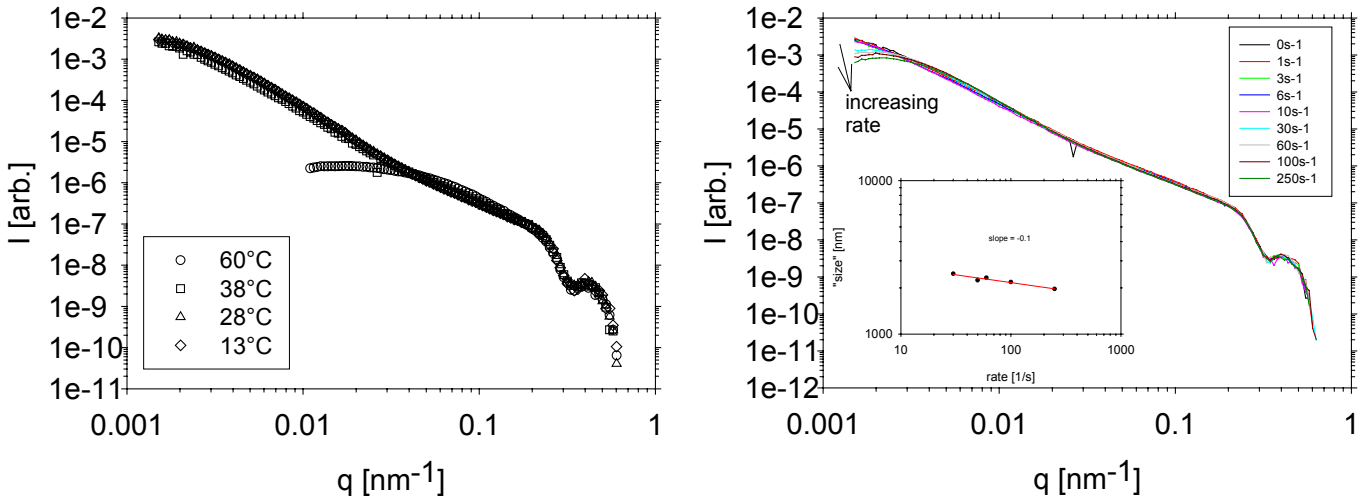

Figure 1a: Quiescent structure of a gelled dispersion of 5% particles (volume) in n-tetradecane measured by USAXS at different temperatures. Figure 1b: USAXS curves at different shear rates and 38.0 °C, the inset shows the floc size, which has only a weak dependance on shear rate.

Light scattering experiments only probe the micron sized length scales in a sample, hence the question remains wheteher the anisotropy is present on all length scales in the sample (from floc size down to particle size) or whether the isotropic fractal concept can be applied to the local scale.

Anisotropy determination from SAXS measurements.

Measurements of the anisotropic structure factor during shear flow were conducted with a 2D SAXS detector. As the observed structure in the SAXS measurements is on a quite local scale (up to 10 particle diameters) the anisotropy in the patterns is not very pronounced. Therefore a method devised by Wagner and Ackerson [4] to analyze weakly anisotropic structure factors during shear flow was used. To calculate the anisotropy the isotropic scattering pattern at rest is subtracted from the scattering pattern during shear flow. The resulting image is then weighed by a cosine function with appropriate symmetry and integrated over the azimuthal angle to obtain the anisotropy. Hence, it is calculated from:

$$A_n = \frac{1}{2\pi}\int_0^{2\pi}\left[I(q,\theta,\dot{\gamma}) - I(q,\theta,\dot{\gamma}=0)\right]\cos(n\theta)\,d\theta \quad .$$

The term with n=2 measures the two-fold anisotropy that is also observed in light scattering experiments. It is displayed in figure 2 for a 5% dispersion. When the shear rate is increased the anisotropy becomes apparent at smaller length scales as indicated by a decrease of the weighed intensity as a function of q. At the higher shear rates it can be observed at length scales as small as three particle diameters. Hence, the two-fold anisotropy persists to almost the smallest relevant length scales in the flocs (the size of an individual particle). It can therefore be concluded that the isotropic fractal concept that is generally used to model the rheological behaviour of this type of materials fails at all length scales. The same type of anisotropy that is observed here is also found in two dimensional aggregated suspensions [5],

where it also persists down to the local length scales. For the 2D case the mechanism that causes the anisotropy to develop is a direction dependence of aggregation and break-up [6].

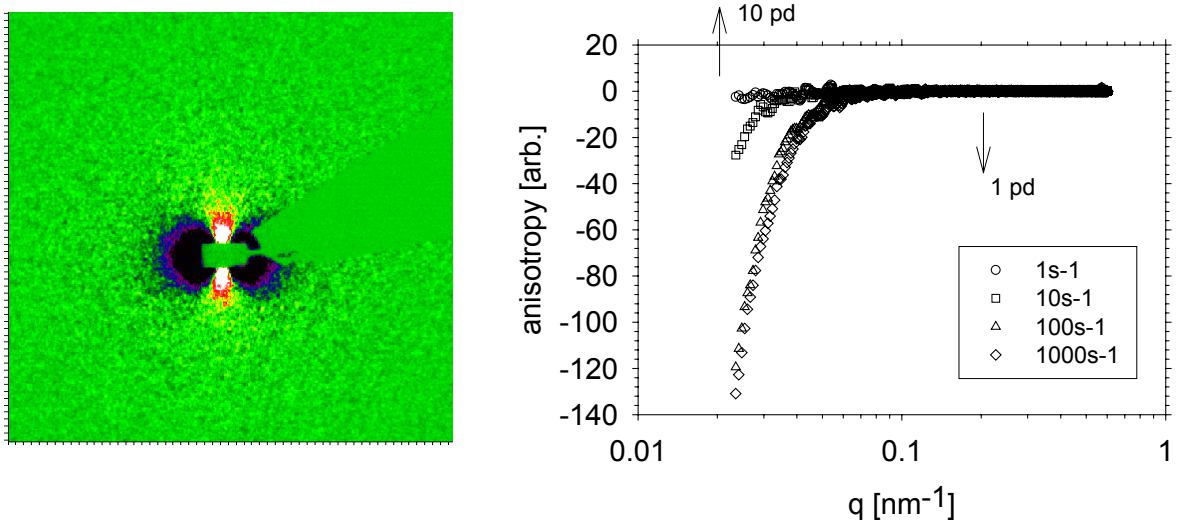

Figure 2a: 2D scattering pattern at a shear rate of 1000 s^{-1} after subtraction of the isotropic rest quiescent structure (5% particles at 38 °C). Figure 2b: Anisotropy from SAXS patterns of a suspension of 5% (volume) particles in n-tetradecane at 38.0 °C. The arrows correspond to 1 and 10 particle diameters.

For all volume fractions investigated in the X-ray experiments a local scale ansotropy is observed that increases with shear rate. When, for each of the samples studied, the degree of undercooling is increased, a more strongly aggregated material results. The structure during shear flow however shows no anisotropy in the shear rate range explored when the quench is too deep (e.g. for the 13°C case in figure 1).

Conclusions

1. The present experiments provide proof for the presence of a shear induced anisotropy in reversibly aggregated sticky sphere suspensions, which persists to the local scale. Hence, simple fractal models of the flocs fail on all length scales in shear flow.
2. Anisotropy in the aggregated state is observed for all volume fractions studied, it disappears when the depth of the temperature quench is increased.
3. The current data set will be combined with SALS data and rheological measurments, providing a benchmark set for thixotropy modelling [7].

References

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