

Nonlinear Rheological Investigations of a Bimodal Mixture of PS-PNIPAm Core-Shell Particles around the Glass Transition

L. Fischer¹, M. Sutharsan², M. Fuchs², M. Wilhelm¹

¹ Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76131 Karlsruhe, Germany
(lea.fischer@kit.edu)

² University of Konstanz (UKN), Universitätsstr. 10, 78464 Konstanz, Germany

Understanding the behaviour of high concentrated colloidal suspension in the glassy state under applied mechanical fields is a long-standing problem in colloid physics. While the linear rheological behaviour of the colloids was thoroughly investigated, there is a lack of understanding the nonlinear rheological behavior. Therefore, we focus on the asymptotically nonlinear behaviour in oscillatory shear measurements, i.e. in the medium amplitude oscillatory shear (MAOS) region and the frequency dependent spectra of the leading nonlinear response.

For this, a polystyrene-poly(N-isopropylacrylamide) (PS-PNIPAm) core-shell system was synthesized according to Dingenouts *et al.*¹ The synthesised system is thermoresponsive, i.e. the hydrodynamic radius R_H and therefore the volume fraction ϕ of the colloids is adjustable *in-situ* by changing the temperature. To suppress the crystallization process, a bimodal mixture of two batches with a size ratio of 1.7 is used.

With this well characterized colloidal suspension a comprehensive rheological study of the glassy state ($\Phi > \Phi_g$) and the fluid state near the glass transition of colloidal suspensions is possible. In previous work the frequency dependent intrinsic nonlinearity parameter Q_0 , which is a measure for the deviation from the linear behavior, of a colloidal suspension in the fluid region near the glass transition was already investigated and compared to mode-coupling theory calculations².

We now extend these measurements in the fluid region to broader frequency ranges. Our results show the same power law behavior of Q_0 , as predicted by mode-coupling theory calculations.² In addition, we extended the nonlinear measurements to the glassy regime, where we investigated a broad range of the frequency dependent spectra by using frequencysweep MAOS introduced by Singh *et al.*³ It was found, that the intrinsic nonlinearity Q_0 for glassy samples is lower for the same Péclet number (Pe) than for the liquidlike samples. For all Pe the ratio of the third harmonic to the fundamental $I_{3/1}$ increases with increasing strain amplitudes γ_0 like expected. For low Pe (e.g. 7.5×10^{-5}), this increase shows a scaling law with an exponent of 4 instead of the expected exponent of 2. The higher exponent results from the increase of I_3 with the power of 5 while the fundamental I_1 still shows the expected power law in this region. To the best of our knowledge, a higher exponent than 3 for I_3 (i.e., a higher exponent than 2 for $I_{3/1}$) has never been reported before. We now plan to investigate this unexpected power law behaviour further to find out the underlying physical behaviour.

¹ N. Dingenouts, *et al.*, *Macromolecules*. **31**, 8912 (1998).

² R. Seyboldt, *et al.*, *Soft Matter*. **12**, 8825 (2016).

³ P. Singh, *et al.* *J. Rheol.* **62**, 277 (2018).