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1 Methods and materials

1.1 Nanoparticle preparation (SPION^{LAc})

Iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) and iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Merck (Darmstadt, Germany). Heavy metal-free dialysis tubes Spectrapor 7 (MWCO 10 kDa) were supplied by Spectrum Labs (Frankfurt, Germany), lauric acid (LA) by AppliChem (Darmstadt, Germany). Ammonium chloride, nitric acid 65 % and ammonia solution 25 % were purchased from Carl Roth (Karlsruhe, Germany). Minisart NML syringe filters (0.8 μm pore size) were supplied by Sartorius (Goettingen, Germany). The water used in all experiments was purified by means of a Siemens Ultra Clear system (Evoqua Water Technologies, Günzburg, Germany).

Synthesis of in situ coated lauric acid SPIONs with high iron concentration (SPION^{LAc})

The synthesis of SPION^{LAc} was performed according to a modified method as described by Zaloga et al.[1] and Bica et al.[2] In short, ultrapure water was used to dissolve iron (II) and (III) salts in a molar ratio of 1:2. The solution was heated up to 90 °C and, while constantly stirring, an argon flow was applied. 25 % NH_3 solution was added to precipitate the iron oxides. Lauric acid dissolved in acetone was added and temperature was maintained for 15 min. After cooling down to room temperature, the brown-black colloid was filtered through 0.8 μm syringe filter and purified by multiple dialysis against ammonia buffer and water. pH was adjusted to 9.0.

Iron Quantification.

The total iron content was routinely determined using an Agilent 4200 microwave plasma-atomic emission spectrometer (MP-AES, Agilent Technologies, Santa Clara, CA). The ferrofluid was diluted in triplicates with ultrapure water. Subsequently, the diluted samples were dissolved in 65 % nitric acid for 10 min at 95 °C. After cooling to room temperature, samples were further diluted with H_2O. The iron content was then determined with MP-AES using a commercial iron solution as external standard. The calibration curve was prepared with iron concentrations ranging from 0.05 mg/l to 5.0 mg/l.

Hydrodynamic Diameter

The hydrodynamic particle diameter in water was measured by dynamic light scattering using a Nanophox (Sympatec, Clausthal-Zellerfeld, Germany). The particles were diluted to a total iron concentration of 175 μg/ml using ultrapure water and measured in triplicates at 25 °C.

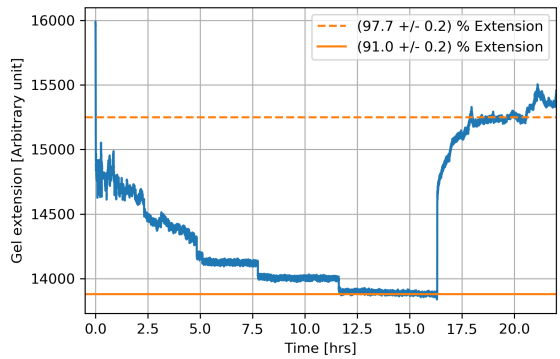
Magnetic Susceptibility

The magnetic susceptibility of the particles was determined in triplicates using a MS2G magnetic susceptibility meter (Bartington Instruments, Oxfordshire, UK) at an iron concentration of 1 mg/ml as described by Unterweger et al.[3]

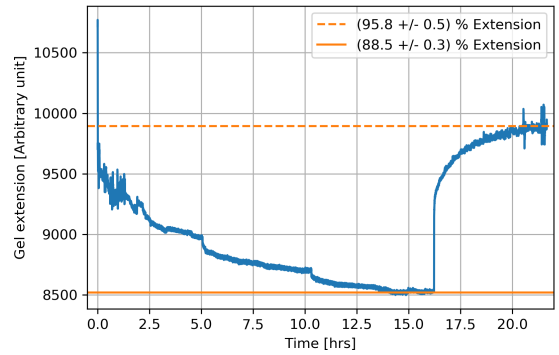
2 Results and discussion

2.1 Ferrogel compression: Discontinuous shape transitions

Ferrogels were compressed within heterogeneous magnetic fields for about 16 hours and their relaxation observed for further six hours. In order to investigate the nature of discontinuous shape transitions during compression comparison measurements with samples in water and in oil were performed. Starting hypothesis was friction as causing variable. The results showed softened steps during compression for the samples measured in oil. Stepwidths were of a similar size as the samples measured in water, though. Steps were thus assumed to be caused by friction.



(a) Strictly angular steps. Measured in water.



(b) Softened steps. Measured in oil.

Fig. 1 Longterm compressions measured in (a)water and (b)oil as surrounding medium to investigate stepwise compressions. We observe steps of the similar size for both measurements. However, samples measured in oil exhibit strongly softened steps. As discontinuous shape transisiont furthermore only occurr during compression and not during relaxation, they are assumed to be caused by friction.

References

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