Supporting Information (SI): In-situ investigation of temperature induced agglomeration in non-polar magnetic nanoparticle dispersions by small angle X-ray scattering

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Figure 1: Isothermal magnetisation measurements at 300 K for samples. The solid line represents a Langevin fit base on equation 1 including.

Magnetic moments of nanoparticles

Magnetic moments of the Fe_3O_4 nanoparticles were measured on dry powder samples. Powders were obtained by evaporating the solvent for 48 h in vacuum at RT from the mixtures used in the SAXS experiments. Isothermal magnetisation measurements were performed at room temperature using a PPMS setup (Physical Properties Measurement System - Quantum Design PPMS-14) with VSM option (Vibrating Sample Magnetometer) in magnetic fields with strengths up to 3 T. Figure 1 shows mass magnetisation [A m²/kg] vs magnetic field strength [A/m].

We fitted the data from the M - H measurement using a Langevin fit (for superparamagnetic nanoparticles) with a linear term that accounts for a paramagnetic background. The solid lines in figure 1 represent fits from our combined model

$$M(H) = M_S \cdot (\coth(x) - 1/x) + p \cdot H \quad \text{with} \quad x = \frac{\mu_{Np}\mu_0 H}{k_B T}$$
(1)

with the saturation magnetisation M_S and the particle moment μ_{Np} . From the fits, we obtain a mass magnetisation of $M_S = 21.74 \,\mathrm{A}\,\mathrm{m}^2/\mathrm{kg}$ and particle moment $\mu_{Np}/\mu_B = 1.05 \cdot 10^4$ for FeNP₁₀ and $M_S = 18.6 \text{ A m}^2/\text{kg}$ and $\mu_{Np}/\mu_B = 5.4 \cdot 10^4$ for FeNP₂₀ with $\mu_B = 9.274 \cdot 10^{-24} \text{J/T}$ (Bohr magneton).

The measurements show that magnetisation curve is not fully saturated at the highest applied magnetic field strength. This may be explained by the paramagnetic background that constitutes the linear term in equation 1. We attribute this observation to the relatively small mass (gravimetric measurement of a few mg), which makes the measurement more prone to paramagnetic background contamination. Errors from the gravimetric measurements directly propagate to the measured mass magnetisation. This may also explain that values reported in literature are typically 1.5-2 times higher for similar nanoparticles than M_S observed by us. Nevertheless, the curvature of the M - H measurement remains unaffected and we may extract the particle moment from the Langevin fit. The model describes the data sufficiently. Introducing the particle size distribution measured by SAXS for μ_{Np} did not further improve the quality of the fit. Deviations between model curve and data are more obvious for FeNP₂₀. We attribute this to the unknown configuration of dried particles in our powder measurement, which affects the curvature of M - H loops quite significantly (see reference *Lucía Gutiérrez et al. 2019 Nanotechnology 30 112001*).

Temperature dependent scattering from toluene

We measured toluene in capillaries with the same wall thickness for a range of different temperatures at small and wide angles with the identical temperature protocol as described in the main manuscript. Results below show that we may consider toluene to give a constant background contribution in the SAXS regime for the investigated temperatures of our data analysis and that no freezing occurs above 123 K.



Figure 2: Left: SAXS data of FeNP_{20} and toluene at different temperatures. Right: WAXS data of supercooled toluene. First diffraction peaks from crystalline toluene are visible at 123 K.