Ordered arrays of nanoparticles show unique behavior which is different from that of the bulk and isolated particles (c.f. [1-4] and references therein). Various techniques making use of spontaneous self assembling have been reported. In the simplest case, a drop of a colloidal nanoparticle solution is applied on a substrate. Subsequently, the process of solvent evaporation induces formation of single or multiple layers resulting in an ordered nanoparticle array.

The iron oxide nanoparticles were synthesized by a high temperature solution phase reaction of metal acetylacetonates (Fe(acac)3) with 1,2 hexadecanediol, oleic acid and oleylamine in phenyl ether [5]. Toluene was used as a solvent. The nanoparticles are single domain due to their small size and behave as single dipoles because the dipole dipole interaction of magnetic iron oxide nanoparticles is weak. The nanoparticles show a well developed crystalline structure and are superparamagnetic at room temperature, the blocking temperature being $T_B=22 \text{ K}$. The 5 µL drops of the colloid solution were deposited onto silicon substrates of 1 cm² area covered with a native SiO² layer. The drops were dried in air at room temperature.

The experiment was performed on the GISAXS beamline BW4 at the Hamburger Synchrotronstrahlungslabor [6]. The size of the focused beam at the substrate position, as determined from 1/e of the maximum intensity, was 65x35 µm² size (horizontal × vertical). The X-ray wavelength was set to 0.138 nm. We employed two measurement modes [7]. In a substrate mode, the substrate was aligned in order to halve the primary beam intensity and subsequently tilted by 0.18° (standard GISAXS alignment with the angle of incidence of 0.18°). In a drop mode, the substrate was vertically translated downwards by 100 µm out of the primary beam after having been aligned and subsequently tilted by 0.1° in order to eliminate the X-ray scattering from the substrate. In this mode, solely the X ray scattering from the drop (including its surface as it was crossing the primary beam during evaporation) was measured. The scattered X-ray radiation was detected by a two dimensional X-ray CCD camera located at the distance of 1971 mm from the substrate. Each CCD pattern was acquired for 2.6 s if not stated otherwise.

In order to visualize the temporal evolution of the GISAXS, we used t-q_y intensity maps [7]. The intensity corresponding to a particular $(t, q_y)$ point is obtained by an integration of the measured intensity over the $q_y$ interval of $<0.22, 0.39>$ nm⁻¹ at a constant $q_y$ in the GISAXS pattern taken at the time instant $t$. In order to quantify the temporal evolution, we integrated further the scattered intensity also over the $q_y$ interval of $<0.6, 0.9>$ nm⁻¹ to obtain a partial integrated scattering (PIS) as a function of time.
Fig. 1a shows the t-q_y map measured in the *substrate mode*. The GISAXS signal comes from the already dried nanoparticles on the substrate, the drop volume and drop surface. Distinct lines at q_y = ±0.8 nm⁻¹ are observable from the early stages, indicating the formation of an ordered nanoparticle array from the very beginning of the detection. The GISAXS signal along the q_y direction increases gradually with time and culminates at t = 120 s when the drop surface crosses and scatters strongly the X-ray beam in the form of a detector scan. The corresponding PIS plot is shown in Fig. 1b. At the beginning, the scattered signal grows linearly while an exponential like increase is observed when the drop surface crosses the primary X-ray beam before escaping from it completely. After this transient, the scattered intensity decreases to a stationary value produced solely by the dried self assembled nanoparticle array on the substrate.

Measurements in the substrate mode cannot distinguish between the signal scattered from the ordered nanoparticle assembly on the substrate surface and on the drop surface. Therefore, we utilized the *drop mode* which probes the drop exclusively. In order to minimize the impact of the read out time on possible short transients, we enhanced the integration time of a single GISAXS pattern from 2.6 s to 13.6 s. The measured t-q_y map and PIS plot are shown in Fig. 2a and Fig. 2b, respectively. Differently to the substrate mode, the t-q_y map shows no ordering lines and the GISAXS signal along q_y decays monotonously with time up to t = 120 s. The linear increase of the PIS plot is dominated by the volume scattering of the linearly densifying drop. The exponential like final increase may be attributed to a combined effect of the volume and surface scattering from the colloidal drop. Finally, the drop escapes from the X-ray beam and the measured scattering signal goes to a background value. No evidence of the existence of ordered nanoparticle arrays in the drop volume or on the drop surface within the employed statistics has an important implication. According to our calculations, approx. 63% of the incident X-ray intensity probed the drop volume located between 82 µm and 118 µm above the substrate surface. Therefore, the self assembly process takes place no more than approx. 80 µm above the substrate surface in the vicinity of the drop contact line.

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**References**