Spatiotemporal Study of Iron Oxide Nanoparticle Monolayer Formation at Liquid/Liquid Interfaces by Using In-Situ Small Angle X-Ray Scattering

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Supporting Information

S1. Schematics of the SAXS cell

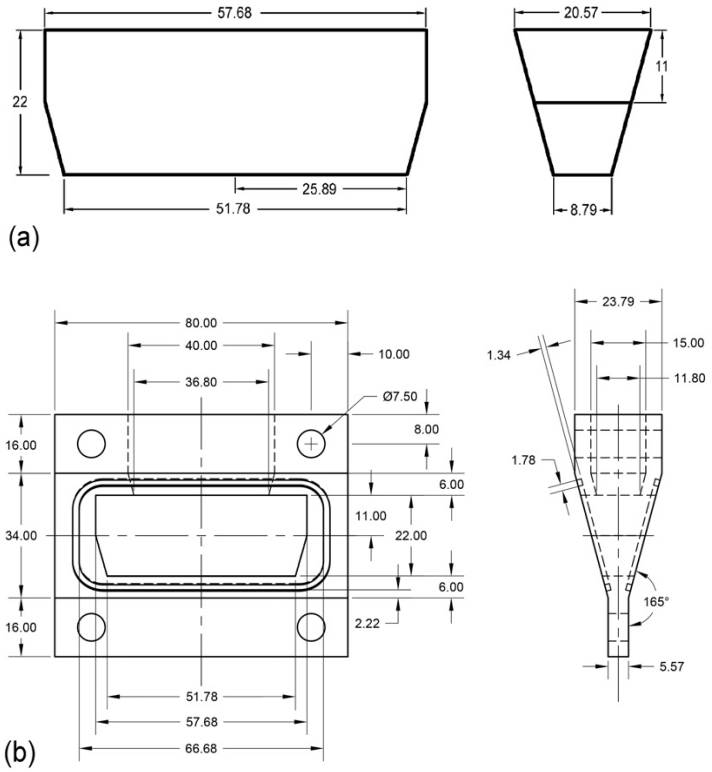

Figure S1. Schematics of the tapered, SAXS cell (the middle part) (also called the sample cell or SAXS sample cell in the main text), with (a) the inside of the cell and (b) an overview, with dimensions in mm.

S2. x-ray beam path and measurement

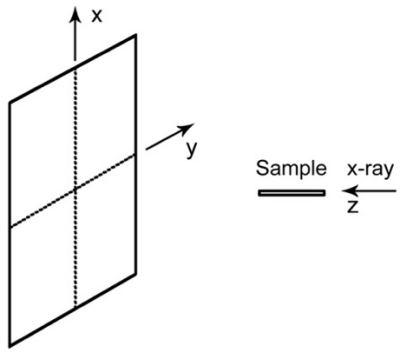

Figure S2. Directions in x-ray probing, with the sample being the SAXS cell. The beam is 200 μm wide in the *y* direction and 50 μm high in the *x* direction.

S3. Calibration of the interfacial coverage of NPs and the numbers of NPs being probed

Calibration

The number of nanoparticles (NPs) drop-cast in the SAXS cell was calibrated in terms of the number of monolayers (MLs) of close packed NPs at the DEG/vapor interface in a Petri dish.

The area of the Petri dish with a diameter of 2.9 cm that was used to calibrate NP concentration is 6.61 cm^2, but it is estimated that with the meniscus the surface area is ~2% larger, or 6.74 cm^2. The area of the flat DEG/vapor interface in the tapered SAXS cell is 1.133 cm (length) × 5.433 cm (width) = 6.16 cm^2, ignoring the corner and side wall menisci. The total area of the concave down DEG/heptane interface in this tapered SAXS cell is 1.22 cm (the length along the meniscus curvature, as depicted in Sections S5 and S6) × 5.40 cm (width) = 6.59 cm^2, again ignoring the corner and side wall menisci.

Using the data in Figures 3b, 4e, 4f and S21, for 8.6 nm NPs the distance between the centers of nearest neighbor cores for close-packed, ordered NP MLs is 10.24 nm at the DEG/vapor interface for drop-casting on a heptane reservoir and after heptane drying and 12.19 ± 0.22 nm at the DEG/heptane interface after drop-casting onto the heptane reservoir on DEG; these correspond to respective areal NP densities ~$1.10 \times 10^{10}/mm^2$ and ~$7.77 \times 10^{9}/mm^2$. For

11.8 nm NPs, these distances are 13.68 nm at the DEG/vapor interface for NPs directly drop-cast on DEG and 15.11 ± 0.33 nm at the DEG/heptane interface for NPs drop-cast into the heptane reservoir on DEG; these correspond to respective areal NP densities ~6.17×10^9/mm^2 and ~5.06×10^9/mm^2. So, the NP concentrations in the drop-cast dispersions for 1 ML-equivalents are ~1.10×10^{10}/mm^2 × 6.74 cm^2/60 μL = 1.24×10^{11}/mm^3 for 8.6 nm NPs and ~6.17×10^9/mm^2 × 6.74 cm^2/60 μL = 6.93×10^{10}/mm^3 for 11.8 nm NPs.

Therefore, the measured 1 ML-equivalent NPs calibrated at the DEG/vapor interface in the Petri dish correspond to ~7.42×10^{12} NPs with 8.6 nm diameter and ~4.16×10^{12} NPs with 11.8 nm diameter. A close-packed NP ML at the DEG/heptane interface includes ~5.12×10^{12} NPs with 8.6 nm diameter and ~3.33×10^{12} NPs with 11.8 nm diameter. This assumes that in each case there are no significant defects in the large patches of ordered NPs at the interface.

Also, in the tapered SAXS cell:

For 8.6 nm NPs:

- 1 ML-equivalent of NPs corresponds to $\frac{\frac{6.74}{10.24^2}}{\frac{6.59}{12.19^2}} = 1.45$ ML of closely packed NPs at the DEG/heptane interface (and so 1 ML of NPs at the DEG/heptane interface in the SAXS cell corresponds to $\frac{\frac{6.59}{12.19^2}}{\frac{6.74}{10.24^2}} = 0.69$ ML at the DEG/vapor interface in the calibration Petri dish).
- 1 ML-equivalent of NPs corresponds to $\frac{6.74}{6.16} = 1.09$ ML at the DEG/vapor interface in the SAXS cell.

For 11.8 nm NPs:

- 1 ML-equivalent of NPs corresponds to $\frac{\frac{6.74}{13.68^2}}{\frac{6.59}{15.11^2}} = 1.25$ ML of closely packed NPs at the DEG/heptane interface; so 1 ML of NPs at the DEG/heptane interface in the SAXS cell corresponds to $\frac{\frac{6.59}{15.11^2}}{\frac{6.74}{13.68^2}} = 0.80$ ML at the DEG/vapor interface in the calibration Petri dish.
- 1 ML-equivalent of NPs corresponds to $\frac{6.74}{6.16} = 1.09$ ML at the DEG/vapor interface in the SAXS cell.

Numbers of NPs being probed

With the beam positioned at the top of the DEG/heptane meniscus i.e., the top 25 μm of the 50-μm-tall x-ray beam is in the heptane and the bottom 25 μm is in the DEG (Figure S6), the

beam probes 200 μm × 3.26 mm ~ 0.65 mm^2 of the interface. For 1 ML coverage of 8.6 nm iron oxide NPs, with hexagonal ordered close packed NPs and a ~12.19 nm distance between core centers, ~ 0.65 mm^2 × (~7.77 × 10^9/mm^2) ~ 5.05 × 10^9 NPs are probed and for the 11.8 nm NPs (~15.11 nm core distance), ~ 0.65 mm^2 × (~5.06 × 10^9/mm^2) ~ 3.29 × 10^9 NPs are probed. Measurement-to-measurement uncertainties during beam repositioning within a run leads to uncertainties in these values, and scatter in the data of the SAXS intensities of ordered and disorder NP signals. For the beam position denoted as just below the meniscus, an area of 200 μm × 4.24 mm ~ 0.85 mm^2 is probed, and ~ 0.85 mm^2 × (~7.77 × 10^9/mm^2) ~ 6.61 × 10^9 of 8.6 nm NPs and ~ 0.85 mm^2 × (~5.06 × 10^9/mm^2) ~ 4.30 × 10^9 of 11.8 nm NPs are analyzed.

When the beam is only in the heptane, just above the meniscus (Figure S5), for 1 ML-equivalent of NPs drop-cast and *remaining* in the dispersion in the probed volume of 50 μm × 200 μm × 11.58 mm = 0.116 mm^3. For 8.6 nm and 11.8 nm NPs, the NP concentrations in the dispersion drop-cast on top of the 1.06 mL of heptane reservoir, including the 60 μL volume of the drop that is cast, are respectively ~ 7.42 × 10^{12}/1,060 mm^3 ~ 7.00 × 10^9/mm^3 and ~ 4.16 × 10^{12}/1,060 mm^3 ~ 3.92 × 10^9/mm^3, and the number of NPs respectively probed are ~ 7.00 × 10^9/mm^3 × 0.116 mm^3 ~ 8.12 × 10^8 and ~ 3.92 × 10^9/mm^3 × 0.116 mm^3 ~ 4.55 × 10^8. At the meniscus, the number of NPs probed in the dispersion are ~ 0.90 × these values.

After heptane removal, the beam probes the flat DEG/vapor interface with ML ordered NPs across the interface, with area 200 μm × 11.33 mm ~ 2.27 mm^2, for 1 ML coverage of 8.6 nm iron oxide NPs, for hexagonal ordered close packed NPs with a 10.2 nm distance between core centers, 8.6 nm NPs ~ 2.27 mm^2 × (~1.10 × 10^{10}/mm^2) ~ 2.50 × 10^{10} NPs are probed and for 11.8 nm NPs ~ 2.27 mm^2 × (~6.17 × 10^9/mm^2) ~ 1.40 × 10^{10} NPs are probed, or ~4-5 times the number probed at the DEG/heptane meniscus.

S4. x-ray beam blocking

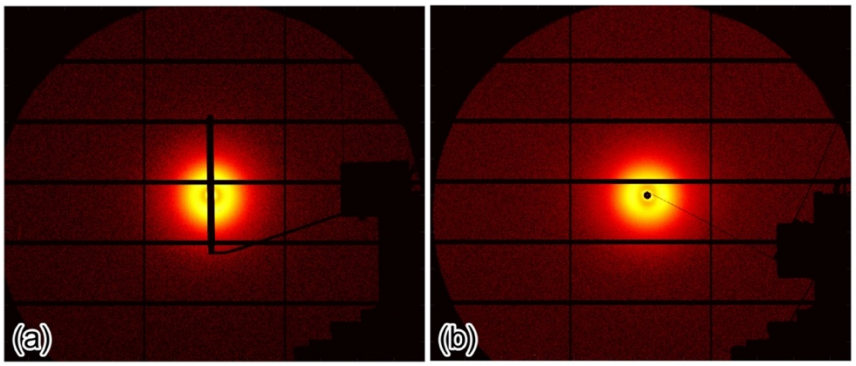

Figure S3. The (a) strip and (b) very small circular beam stops used front of the x-ray detector in the SAXS measurements are seen in the center in black.

S5. DEG/heptane meniscus shape and x-ray transmission (without NPs)

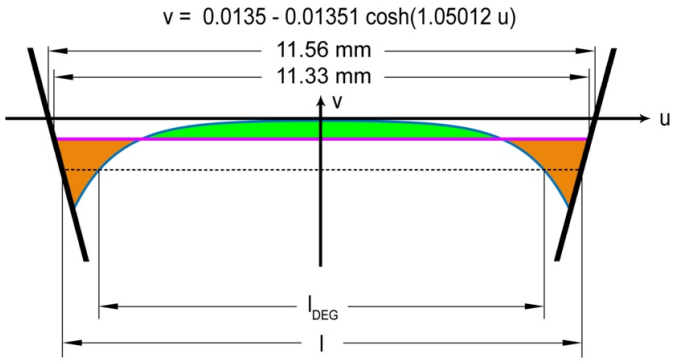

Figure S4. DEG in the tapered SAXS, below the violet line before adding heptane and below the blue curve after adding heptane. The green and orange areas are the same–ignoring the effects of the menisci corners in the cell.

The blue curve is the DEG/heptane meniscus in the tapered SAXS cell. The top of the curve is tangent at the origin. The meniscus curve is at $v < 0$, and includes the green and not the orange region. At the top of the meniscus, the x-ray path length through pure heptane is 11.56 mm; 50 µm above it, the path length is 11.58 mm. The violet line shows the location of the

DEG/vapor interface when there is no heptane layer above the DEG, and includes the orange and not the green region; it is 11.33 mm long.

This DEG/heptane meniscus shape is measured using x-ray transmission. At any position of x-ray beam height relative to the cell of *v*, the transmitted x-ray intensity between the two windows divided by that with no solvent present, which in both cases includes scattering from the windows, is the transmission *T*:

$$T(v) = \frac{I(v)}{I_{air}}.$$

The absorption coefficients α in the two liquids are:

$$\alpha_{DEG} = 164.3/\text{m};$$
$$\alpha_{heptane} = 55.94/\text{m};$$

At the top of this meniscus $v = 0$, the x-ray beam propagates through pure heptane, so $T(0) = e^{-\alpha_{hep} l(0)}$, and therefore $l(0) = l_{pure\ hep} = -\frac{lnT(0)}{\alpha_{hep}} = 11.56$ mm. The windows are tilted at 75°, so the total x-ray path length is

$$l(v) = l(0) + 2v\ cot(75°).$$

Below the top of the meniscus, $v < 0$, the beam propagates through heptane and DEG, and the transmission is

$$T = e^{-\alpha_{hep}(l - l_{DEG}) - \alpha_{DEG} l_{DEG}}.$$

Therefore,

$$l_{DEG} = \frac{lnT + \alpha_{hep} l}{\alpha_{hep} - \alpha_{DEG}},$$

where l_{DEG} is the path length of the beam in the DEG for a given v of the beam relative to the top of the meniscus. The curve is fit to the x-ray transmission data by a hyperbolic function, giving the meniscus shape that is plotted above:

$$v = 0.0135 - 0.01351\, cosh(1.05012u).$$

The height of the DEG/heptane meniscus is 1.90 mm. The arc length is 1.22 cm and the meniscus length 5.40 cm, so the total area of the concave down DEG/heptane interface in this tapered SAXS cell is 6.59 cm^2, ignoring the corner and side wall menisci.

S6. x-ray beam height relative to the meniscus

The x-ray beam positions relative to the DEG/heptane meniscus is described, along with x-ray transmission at each position, using the meniscus shape as given in Figure S4 in Section S5. The sequence of the three beam positions within each repeated cycle is also given below.

Positioning and x-ray transmission

The x-ray beam has a height of 50 μm, so when determining the location of the top of DEG/heptane meniscus, the spatial resolution is 50 μm. (The position of the center of the beam has an error range of 50 μm at the vertical direction.) Figures S5-S7 are diagrams showing three locations: just above, at and just below the top of the DEG/heptane meniscus. Figure S5 is the lower limit of the ***just above*** location; Figure S7 is the upper limit of the ***just below*** location.

Figure S5 shows the x-ray beam ***just above*** the top of DEG/heptane meniscus, by 25 μm. The beam does not pass through the DEG, and does not probe NPs at the DEG/heptane interface.

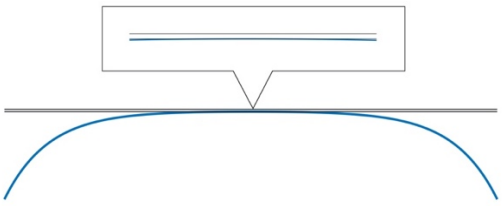

Figure S5. SAXS probing just above the top of the DEG/heptane meniscus, the blue curve. This sketch is drawn to scale.

For this position, the transmission of the beam is:

$$T_{just\ above} = e^{-\alpha_{hep} \cdot 11.58\ \mathrm{mm}} = 52.32\%.$$

Figure S6 shows the x-ray beam half way in both solvents ***at the*** top of the DEG/heptane meniscus; the 25 μm of the top of the beam is in heptane and the bottom 25 μm is in DEG at the meniscus center.

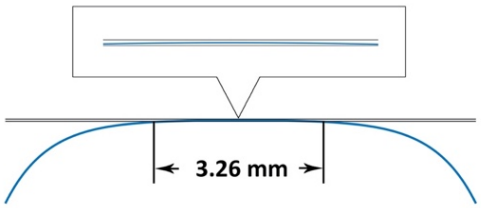

Figure S6. SAXS probing the top of the DEG/heptane meniscus, the blue curve. This sketch is drawn to scale.

For this position, the transmission of the beam is:

$$T_{at\ the\ top} = \frac{25\ \mu\mathrm{m}}{50\ \mu\mathrm{m}} \cdot e^{-\alpha_{hep} \cdot 11.56\ \mathrm{mm}} \times \int_{-25\ \mu\mathrm{m}}^{0} e^{-\alpha_{hep}(11.56\ \mathrm{mm} - 2|u|) - \alpha_{DEG} \cdot 2|u|} \frac{dv}{50\ \mu\mathrm{m}} = 46.84\%,.$$

with *u* and *v* defined in Figure S4. The x-ray transmission is less at this position even with no NPs being probed, and the path length in the DEG is 3.26 mm, which is essentially the arc length of the curved interface with NPs being probed here.

From the side, the total area of the x-ray beam probing the top of the DEG/heptane meniscus is seen to be $11.56\ \mathrm{mm} \times 50\ \mu\mathrm{m} = 0.5780\ \mathrm{mm}^2$. The part of this area in the DEG is $\int_{-3.26\ \mathrm{mm}/2}^{+3.26\ \mathrm{mm}/2} v du - 3.26\ \mathrm{mm} \times v(3.26\ \mathrm{mm}/2) = 0.0570\ \mathrm{mm}^2$. In both cases, the associated volume is this area times the beam width, so the ratio of the volume probed within the NP heptane dispersion to the whole probed region is $(0.5780 - 0.0570)/0.5780 = 90.14\%$, which is used in the text as ~90%.

Figure S7 shows the x-ray beam ***just below*** the top of the DEG/heptane meniscus, by 25 μm.

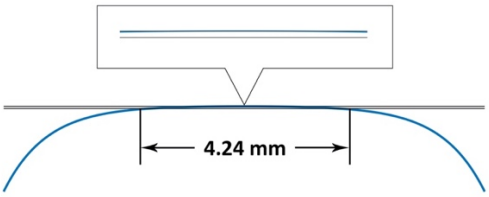

Figure S7. SAXS probing just below the top of the DEG/heptane meniscus, the blue curve. This sketch is drawn to scale.

For this position, the transmission of the beam is:

$$T_{just\ below} = \int_{-50\ \mu m}^{0} e^{-\alpha_{hep}(11.56\ \mathrm{mm} - 2|u|) - \alpha_{DEG} \cdot 2|u|} \frac{dv}{50\ \mu m} = 37.80\%$$

The x-ray transmission is even less at this position even with no NPs being probed, and the path length in the DEG is 4.24 mm, which is essentially the arc length of the curved interface with NPs being probed here.

Cell locations during a cycle

The cycle positioning relative to the meniscus is illustrated in Figure S8:

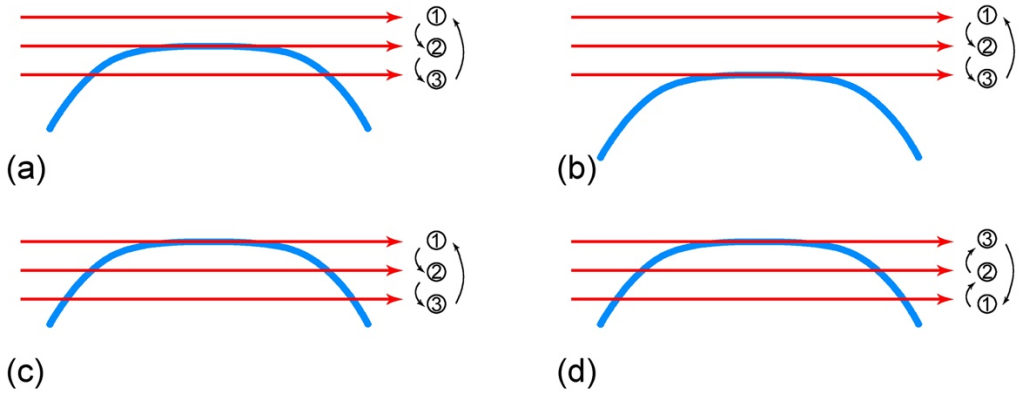

Figure S8. Cell positions during the cycles in a scan. The red arrow is the x-ray beam, the blue curve is the DEG/heptane meniscus, and the numbers in circles and the black arrows show the order of cell locations during a cycle.

For the corresponding cycle positions within in this figure:

(a) As noted in the main text, in the 8.6 nm NPs runs with 1, 3, and 12 ML-equivalents drop-cast, the first SAXS measurement was with the center of the beam 50 μm above the meniscus; then the cell was raised by 50 μm, so the 50-μm tall beam was relatively lowered by this amount and was then "at" the top of the DEG/heptane meniscus; then the cell was raised by 50 μm so the center of the beam was 50 μm below the interface; and then the cell was lowered by 100 μm and the above/at/below the meniscus sequence was repeated again and again.

(b) In the 8.6 nm NPs runs with 0.5 and 9 ML-equivalents drop-cast and the 11.8 nm NPs run with 6 ML-equivalents drop-cast, the cycle began 100 μm above the top of the meniscus, continued 50 μm above it, then at the top, then 100 μm above it again, 50 μm above it again, at the top again, and so on.

(c) In the 8.6 nm NPs run with 6 ML-equivalents drop-cast, the cycle began at the top of the meniscus, then 50 μm below it, 100 μm below it, then at the top again, 50 μm below it again, 100 μm below it again, and so on. So, in Figure 5a, there are no data for the 6 ML-equivalent run of 8.6 nm NPs.

(d) For the preliminary runs with 1, 9, and 18 ML-equivalents of 11.8 nm NPs drop-cast, the cycle began 100 μm below the top of the meniscus, then 50 μm below it, at the top, then 100 μm below it again, 50 μm below it again, at the top again, and so on. So, in Figure 5b there are no data for these runs.

S7. NP form factors

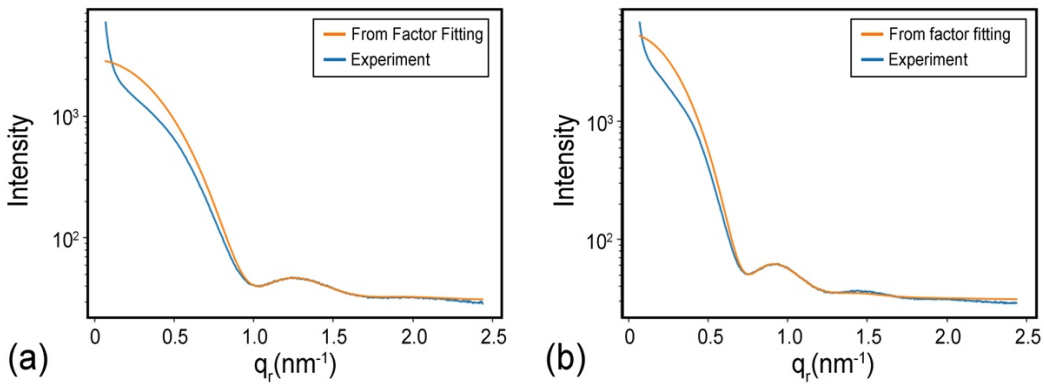

Figure S9. The measured form factors for free dispersed NPs for (a) 8.6 nm and (b) 11.8 nm NPs, with the data in blue and the fit in orange.

The form factors were obtained in separate runs, in a narrow capillary with much higher NP concentrations to increase the signal/noise ratio, using the procedure outlined in Ref. S1. The scattered intensity is: $I(q) \propto \int F(x,q) f(x,\mu,\sigma) x^6 dx$, where the form factor is $F(x,q) = \left|\frac{4\pi}{q^3x^3}\left[sin\left(\frac{qx}{2}\right) - \frac{qx}{2}cos\left(\frac{qx}{2}\right)\right]\right|^2$ for spherical NPs with wavevector q and the diameter x; the assumed gaussian distribution of NP diameters is $f(x,\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$.

S8. SAXS below the meniscus

In the SAXS images in Figure 1c, within Section IV, there are the form factor and the curved sharp peaks that indicate an ordered one NP ML on a tilted interface, as seen in part D and at the bottom of the DEG/heptane interface (the Section IV/V boundary), the sharp peaks are elliptical and nearly circular, because the interface angle is steep, as is seen in part E; this is due to merging of the straight (10) scattering peaks from a flat layer of hexagonally-ordered NPs. This is seen in more detail in Figure S10, top and bottom, respectively (8.6 nm NPs, 1 ML-equivalent). These 1st order patterns have four-fold symmetry, and the bottom halves of the fits to them are shown by the green dots that have been added.

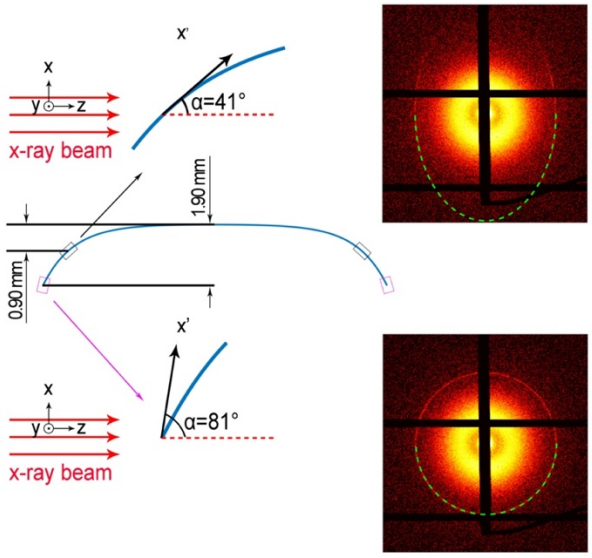

Figure S10. (top and bottom) images D and E in Figure 1c (main text), with SAXS images on the right for the locations denoted on the left. There are green dot fits added to the now curved ordered NP streaks in the SAXS images of each, along with the associated diagrams on the left showing the paths of scattered x-rays relative to the DEG/heptane meniscus, in blue.

The top diagrams show the SAXS profile and location at one place in Section IV, as denoted in Figure 1 in the main text, 0.9 mm below the top of the DEG/heptane meniscus (small tilted black dash line rectangle, with a black arrow showing this region enlarged). The bottom diagrams show these for one place at the bottom of the meniscus, 1.90 mm below the top of the meniscus (small tilted violet dash line rectangle, with a violet arrow showing this region enlarged). A coordinate system (y', x') is attached to the ML plane. The angle between the x-ray beam and the ML plane is α. The equation in sample coordinates $q_{y'}{}^2 + q_{x'}{}^2 = q_{hk}{}^2$ is transformed to $q_y{}^2 + (q_x \sin\alpha)^2 = q_{hk}{}^2$ in laboratory coordinates (y, x).[S2] So, the vertical-streak pattern of the close packed hexagonal ML on a horizontal surface is an elliptical pattern on a slope. The green dash line shown is the fit to the elliptical pattern and gives the angle of the plane. The upper SAXS image is taken at a 41° slope, and the lower one at an 81° slope.

S9. More details about SAXS data analysis

Before each run was started, there was a fit scan to determine the liquid-liquid interface. The fit scan intensity of each run is used to normalize all the data in that run. Between runs, x-ray intensities could have been different because of the different visits and the sensitive x-ray position at the liquid interface.

All the 8.6 nm runs (0.5, 1, 3, 6, 9, 12 ML-equivalents) and one 11.8 nm run (6 ML-equivalents) were performed in one visit to NSLS-II in which a strip beam stop (Figure S3a) was used and the exposure time for each datum point was 5 s. Most of the 11.8 nm runs (1, 9, 18 ML-equivalents) were performed in an earlier visit, in which a very small circular beam stop (Figure S3b) and the exposure time for each datum point was 1 s. The form factor signal is much weaker than the structure factor signal. Furthermore, the use of the very small circular beam stop leads to larger noise due to the larger x-ray background.

The range of 1.057-1.598 nm^{-1} is used for form factor peak fitting for the 8.6 nm NP runs and 0.745-1.150 nm^{-1} is used for the 11.8 nm NP runs. For each of the 8.6 nm runs and the 6 ML-equivalent run of 11.8 nm NPs, an empty data image was taken near the top of the DEG/heptane meniscus before NPs were drop-cast. When fitting the form factor peaks for the 8.6 nm NP data points, this normalized "real", measured background is removed. Uncertainties come from the scanning intensities at the beam facility and stage movement errors, which are important because of large x-ray absorption from DEG. For the preliminary 11.8 nm NP runs (1,

9, 18 ML-equivalents, with the short x-ray exposure time of 1 s), the earliest SAXS images were complete before the NPs were drop-cast, and were used as backgrounds after normalization.

Gaussian functions are used to fit the sharp peaks from the ordered NP ML after the background is removed.

S10. Time of the first collected SAXS data at the DEG/heptane interface relative to drop-casting

The data in Figures 4-8 (main paper) and Figures S11, S12, and S16-S18 are plotted at the end of the period at a position, relative to the $t = 0$ drop-cast time.

In the below tables, the first set of column labels apply throughout.

For the 5 s long x-ray exposures
(with 8 s long periods, each with 5 s exposure + 3 s positioning)

8.6 nm NPs

	First datum point (as seen in Figures 4 a and b)	First time (10) peak appeared (as seen in Figures 4 c-f and 6-8, and Figures S11 and S12)	First datum point (as seen in Figure 5)
0.5 ML-equivalents	19.8 s	43.8 s	11.8 s
1 ML-equivalent	10.0 s	58.0 s	26.0 s
3 ML-equivalents	10.4 s	34.4 s	26.4 s
6 ML-equivalents	2.1 s*	50.2 s	
9 ML-equivalents	18.5 s	42.6 s	2.5 s*
12 ML-equivalents	9.2 s	58.2 s	25.2 s

* Only the first datum point of the SAXS measurement was before the NPs were drop-cast, but the x-ray exposure of NPs was still possible, because the auto drop-casting took 2 or 3 s and the first droplet of NPs could arrive at the DEG/heptane interface before drop-casting finished.

11.8 nm NPs

6 ML-equivalents	17.4 s	41.4 s	25.4 s

For the 1 s long x-ray exposures:
(with 4 s long periods, each with 1 s exposure + 3 s positioning)

11.8 nm NPs

1 ML-equivalent	6.8 s	30.7 s
9 ML-equivalents	6.9 s	22.0 s
18 ML-equivalents	5.6 s	18.6 s

Runs with different heptane reservoir volumes.
(with 6 s long periods, each with 1 s exposure + 5 s positioning)

11.8 nm NPs, 6 ML-equivalents

	First datum point (as seen in Figures S16 – S18)
0.5 mL heptane reservoir	16.1 s
1.0 mL heptane reservoir	5.1 s*
2.0 mL heptane reservoir	6.8 s
4.0 mL heptane reservoir	18.7 s

* The first datum point in the 1.0 mL run does not have x-ray exposure throughout the SAXS measurement, and so it has a very weak peak.

S11. Areal density of the ordered NPs at the DEG/heptane meniscus vs. time

In the 2D hcp packing ML structure, the NP core center to core center distance $d_{NP-NP} = \frac{2\pi}{q_{10}} \times \frac{2}{\sqrt{3}}$, where q_{10} is the (10) peak wavevector, as plotted in Figures 4e and f in the main paper. The NP areal density $\rho_{NP}^{areal} = \frac{1/2}{\frac{d_{NP-NP}}{2} \times \frac{\sqrt{3} d_{NP-NP}}{2}} = \frac{\sqrt{3}}{8\pi^2} {q_{10}}^2$, is plotted in Figure S11.

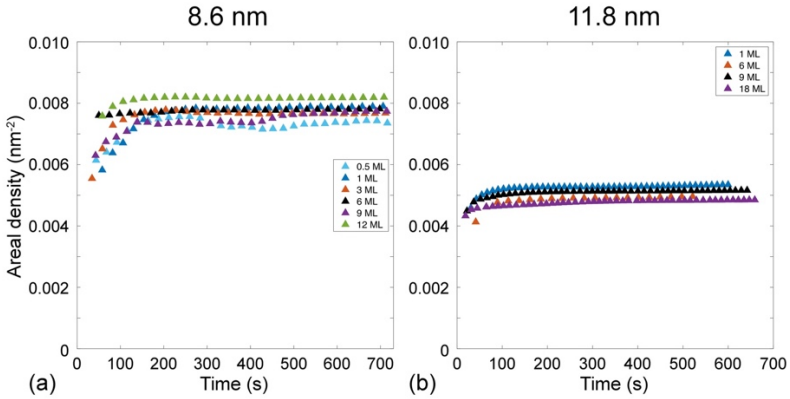

Figure S11. The area densities in 1/nm^2 of ordered NPs at the DEG/heptane interface, for (a) 8.6 nm and (b) 11.8 nm NPs.

Using the data at the end of the run, at ~12 min, the core center-core center separations of 8.6 nm NPs separation at the equilibrium state are for: 0.5 ML (equivalents drop-cast), 12.53 nm; 1 ML, 12.09 nm; 3 ML, 12.26 nm; 6 ML, 12.16 nm; 9 ML, 12.22 nm; and 12 ML, 11.87 nm–for an average separation of 12.19 ± 0.22 nm. This corresponds to an approximate average areal density of ~0.0078/nm^2.

Using the data at the end of the run, at ~10 min, the core center-core center separations of 11.8 nm NPs separation are for: 1 ML, 14.72 nm; 6 ML, 15.27 nm; 9 ML, 14.99 nm; 18 ML, 15.47 nm–for an average separation of 15.11 ± 0.33 nm. This corresponds to an approximate average areal density of ~0.0051/nm^2.

The variations in these areal densities between runs with different amounts drop-cast can be due in part to variations in surface ligand density.

S12. Widths of the ordered SAXS peaks at the DEG/heptane meniscus vs. time

Figure S12 shows the evolution of the peak widths of the (10) peaks of ordered NPs for the data set given in Figure 4 in the main paper.

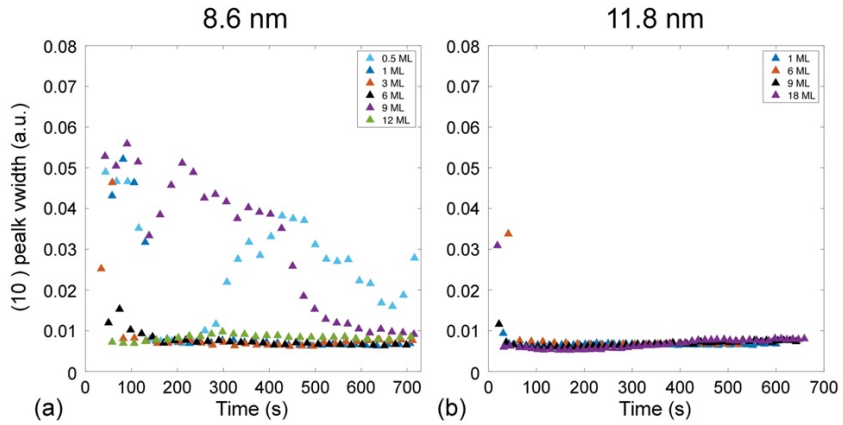

Figure S12. The SAXS peak widths of the (10) peaks for (a) 8.6 nm and (b) 11.8 nm NPs at the DEG/heptane interface for the data set given in Figure 4 in the main paper.

S13. Fitting the ordered SAXS peaks at the DEG/heptane meniscus with two gaussian lineshapes

In Figures 4c-f of the main text, the sharp (10) SAXS peaks for 8.6 nm and 11.8 nm NP runs were fit with a single gaussian peak. Fits using two gaussian lineshapes were discussed in Section 3.5 in the main text and presented in Figures 6-8. Examples of SAXS data and fits are presented here in Figures S13 and S14. Because the fitting procedures were different, the integrated streak areas in Figures 4c and d of the main text are different from the areas of each peak presented in Figure 8, and their sums.

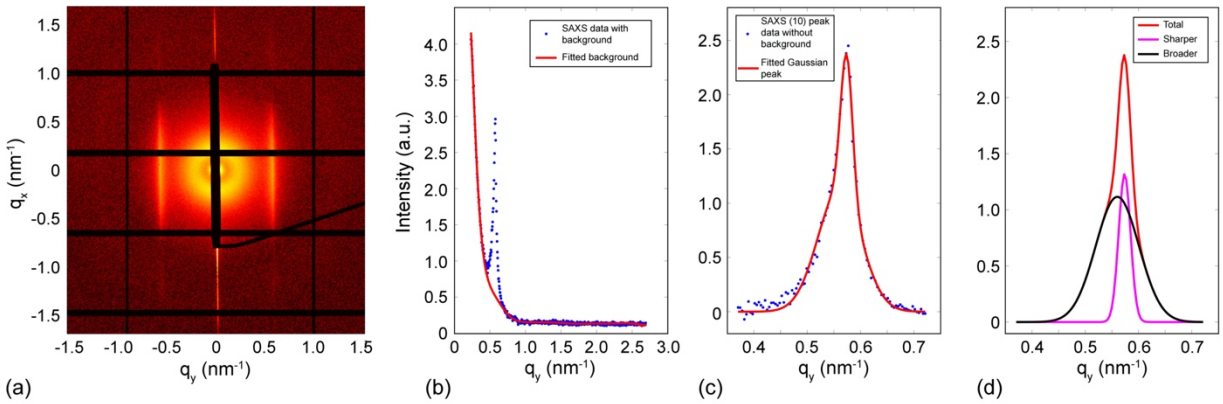

Figure S13: For the 8.6 nm NP run with 0.5 ML-equivalents drop-cast: (a) SAXS image at t = 115.9 s, (b) SAXS data with background in blue dots (horizontal line cut, integrated along q_x from -0.0780 nm^{-1} to +0.0780 nm^{-1}) and the fit to the background in red, (c) the (10) peak data with the background subtracted in blue dots and the two gaussian lineshapes fit in red, (d) the plot of the sum of the two gaussian lineshapes fit in red, with the two single gaussian lineshapes in violet and black. Fits to the ordered peak positions, widths, and areas when using two gaussian lineshapes are included in Figures 6-8 in the main text (in the six panels for the 8.6 nm NPs).

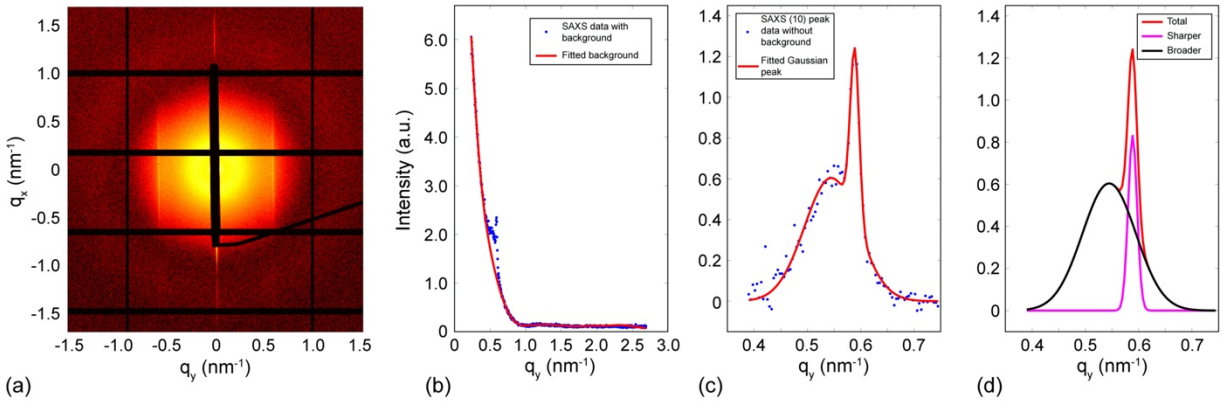

Figure S14: For the 8.6 nm NP run with 9 ML-equivalents drop-cast: (a) SAXS image at t = 114.6 s, (b) SAXS data with background in blue dots (horizontal line cut, integrated along q_x from -0.0780 nm^{-1} to +0.0780 nm^{-1}) and the fit to the background in red, (c) the (10) peak data with the background subtracted in blue dots and the two gaussian lineshapes fit in red, (d) the plot of the sum of the two gaussian lineshapes fit in red, with the two single gaussian lineshapes in violet and black. Fits to the ordered peak positions, widths, and areas when using two gaussian lineshapes are included Figures 6-8 in the main text (in the six panels for the 8.6 nm NPs).

S14. SAXS measurements above the DEG/heptane meniscus

Figure 5 in the main text shows SAXS images taken 50 μm above the meniscus, during the cycling of positions. The NPs were drop-cast at $t = 0$. The first data points are described in Section S10. Unlike at the top of the meniscus where the form factor intensity drops before it reaches equilibrium, the form factor intensities 50 μm above the meniscus for the 9 and 12 ML-equivalents runs have a quick and slight drop before they increase to a steady state. This is probably because most of the NPs that have moved to this detected position reach the meniscus, which leads to a decreased number of NPs there initially, which increase to a steady-state value later. The more NP ML-equivalents drop-cast, generally the higher the steady-state value.

S15. Contact lines

As noted in the main text, it is expected that some NPs in the heptane dispersion migrate to the contact lines between the DEG/heptane and heptane/vapor menisci with the cell windows and walls, and deposit there, as is shown in the photo Figure S15 that was taken to examine this. Here, 11.8 nm 1 ML-equivalent of NPs were drop-cast into the reservoir of 1.0 mL heptane atop the DEG layer in the SAXS cell. Nitrogen was flowed laterally over the uncovered top of the SAXS cell to reduce the air pressure to accelerate the evaporation of heptane. The NPs deposited on the contact lines appear to remain unchanged during the evaporation.

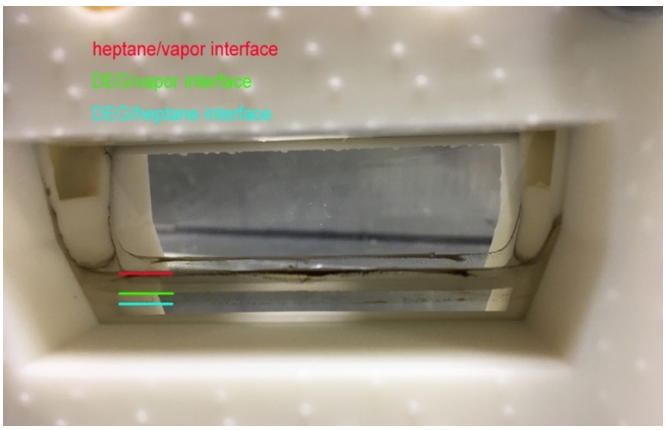

Figure S15. Contact lines of NP deposition, after the upper heptane layer was dried. The red line is the position of the previous heptane/vapor interface contact line. The blue line is the position of the previous DEG/heptane interface contact line. The green line is the current DEG/vapor interface contact line.

S16. SAXS after NP drop-casting on different heptane reservoirs, atop DEG

As described in the main paper, 60 µL of a dispersion containing 6 ML-equivalents of 11.8 nm NPs were drop-cast onto 0.5 mL, 1.0 mL, 2.0 mL, and then 4.0 mL heptane layer on 2 mL DEG, at the same NSLS-II visit. SAXS measurements for the 1.0 mL and 2.0 mL runs were 50 µm above, at the top and 50 µm below the meniscus. For the 0.5 mL and 4.0 mL they are at the top, 50 µm below the top and 100 µm below the top. The SAXS data taken at the top of the DEG are shown in Figures S16-S18. In this set of runs, we set the beam wavelength to be 0.7749 Å (16 keV) to optimize flux; this wavelength is different than that used in other runs and did not change the interpretation of the results.

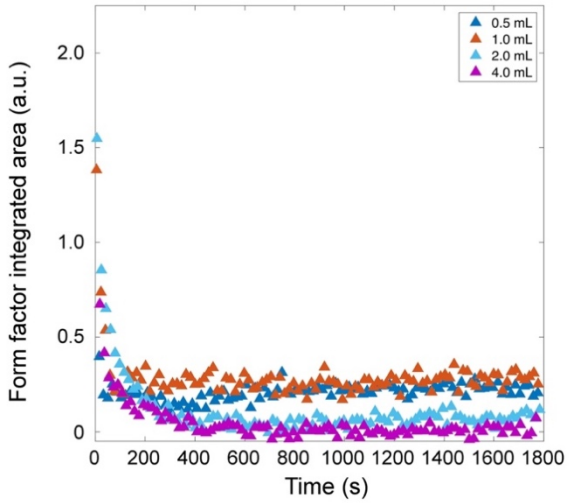

Figure S16. The form factors integrated from 0.745-1.150 nm^{-1} vs. time in the center of and at the top of the DEG layer after 6 ML-equivalents of 11.8 nm NPs are drop-cast on heptane reservoirs of different volumes, atop DEG.

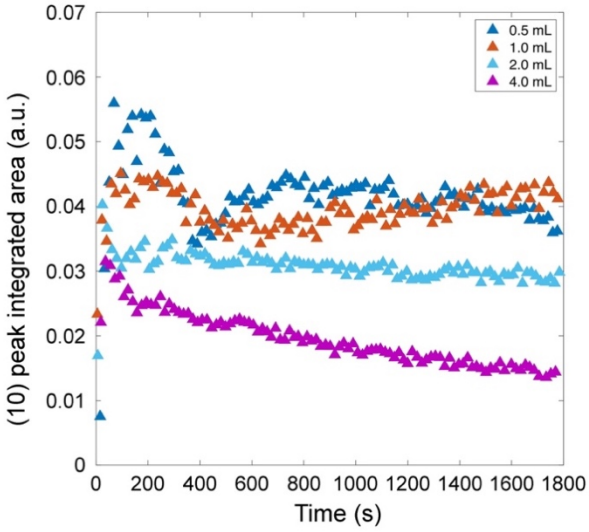

Figure S17. The integrated areas of the (10) peak of the ordered NP ML vs. time in the center of and at the top of the DEG layer, after 6 ML-equivalents of 11.8 nm NPs are drop-cast on heptane reservoirs of different volumes, atop DEG.

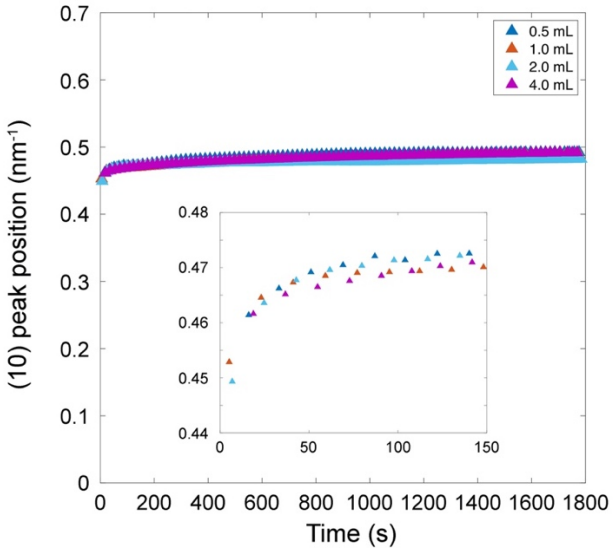

Figure S18. The wavevector of the (10) peak of the ordered NP ML vs. time in the center of and at the top of the DEG layer, after 6 ML-equivalents of 11.8 nm NPs are drop-cast on heptane reservoirs of different volumes, atop DEG.

Each datum point is plotted at the end of the 6 s time at the DEG/heptane interface (1 s exposure time and 5 s processing time). The first datum point of each run is given in Section S10. The 1.0 mL run shows a peak at 5.1 s, even though the exposure time and processing time

are 6 s; maybe this occurred because the auto drop-casting takes 2 or 3 s and the first drop of NP can self-assemble at the DEG/heptane interface before drop-casting finishes. Each run lasted for 30 min.

As noted in the text, x-ray transmission (Figure S19a, below) suggests that for the 0.5 mL run, the heptane resides in the periphery, as depicted in Figure S20 (below). It is also representative after the NP dispersion is drop-cast. The separation of NP in the ordered layer atop DEG, suggests there is a very thin heptane layer there.

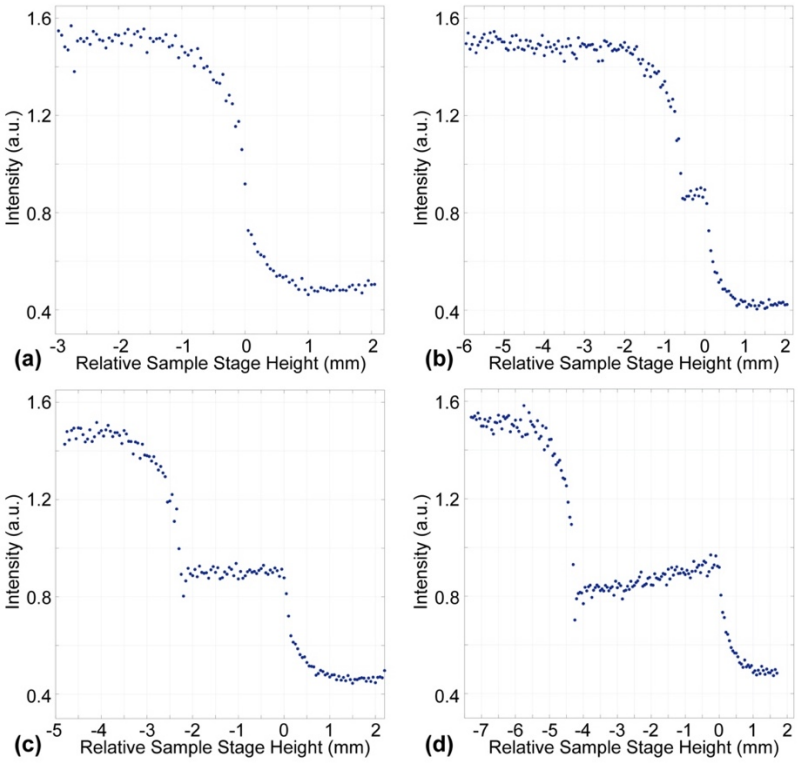

Figure S19. X-ray transmission vs. height, relative to the top of the DEG meniscus, after (a) 0.5 mL, (b) 1.0 mL, (c) 2.0 mL and (d) 4.0 mL of heptane is drop-cast on 2 mL DEG, and before 60 μL of 6 ML-equivalents of 11.8 nm NPs are drop-cast. The distance between the bottom of the heptane/vapor meniscus and the top of the DEG/heptane meniscus for each case is 0, 0.55 mm, 2.10 mm, and 4.25 mm.

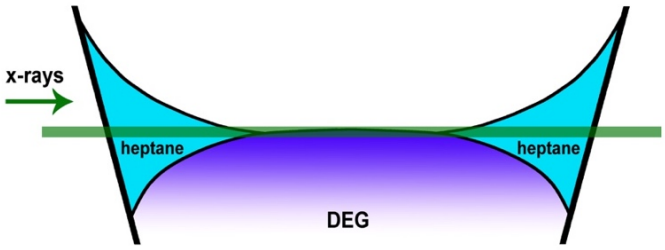

Figure S20. Schematic of DEG/heptane interface for the 0.5 mL heptane reservoir.

S17. Direct drop casting of NPs on DEG

Figure S21a shows the SAXS image after 1 ML-equivalent of 11.8 nm iron oxide NPs in 20 µL heptane was directly drop-cast, by hand dropping and not auto-injecting, on a flat DEG/vapor interface, with an exposure time of 120 s and using the very small circular beam stop. It shows close-packed hexagonal structure with sharp peaks. The (10) peak is 140 pixels from the center, which means $q_y = 0.5458$ nm^{-1}, and a nearest-neighbor core-core separation 13.29 nm, corresponding to a surface-surface separation 1.53 nm. The broken streaks are due to the zeroes in the form factor (Figure S9b), as seen in our previous work (Figures 3a and b, Ref. S3).

For comparison, Figure S21b, shows the SAXS image after 60 µL of 1 ML of 11.8 nm NPs are drop-cast on to 1.0 mL heptane reservoir and forced to dry by using N_2, in ~70 min, with an exposure time of 60 s and using the strip beam stop. The (10) peak is 137 pixels from the center, which means $q_y = 0.5341$ nm^{-1}, and a nearest-neighbor core-core separation 13.58 nm, corresponding to a surface-surface separation of 1.82 nm. The NP separation here is about the same as after direct drop-casting on DEG, but the peaks are broader.

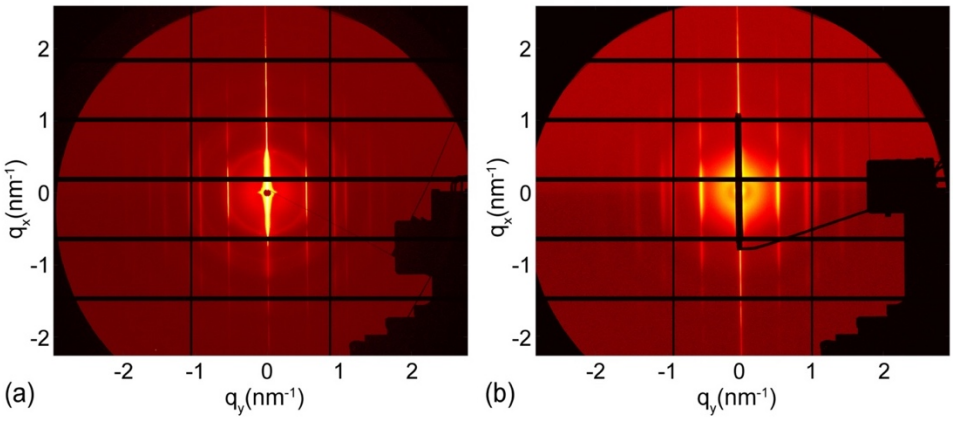

Figure S21. (a) SAXS image after 1ML-equivalent of 11.8 nm iron oxide NPs in 20 µL heptane was directly drop-cast on a flat DEG/vapor interface, (b) SAXS image after 60 µL of 1 ML of 11.8 nm NP heptane dispersion are drop-cast on to a 1.0 mL heptane reservoir and forced to dry by using N_2.

References

S1. Zhang, D.; Lu, C.; Hu, J.; Lee, S. W.; Ye, F.; Herman, I. P. Small Angle X-Ray Scattering of Iron Oxide Nanoparticle Monolayers Formed on a Liquid Surface. *J. Phys. Chem. C* 2015, *119*, 10727-10733.

S2. Narayanan, S.; Wang, J.; Lin, X.-M. Dynamical Self-Assembly of Nanocrystal Superlattices During Colloidal Droplet Evaporation by in Situ Small Angle X-Ray Scattering. *Phys. Rev. Lett.* 2004, *93*, 135503.

S3. Hu, J.; Spotte-Smith, E. W.; Pan, B.; Herman, I. P. Improved Small-Angle X-Ray Scattering of Nanoparticle Self-Assembly Using a Cell with a Flat Liquid Surface. *J. Nanoparticle Res.* 2019, *21*, 71.