We would like to thank both reviewers again for their fast review and their suggestions for how to improve further our manuscript. For a detailed point-by-point response, please see below. Reviewers' comments are copied from your email, our comments start with "Our response:", and the description of what we have changed with "Our alteration:". The changes introduced by us are marked in the revised manuscript with a yellow background.

Reviewer One:

An interesting manuscript to revisit. The technical difficulty of this experiment is underlined by the scepticism of my fellow reviewer to the experimental method and conclusions. The authors reply is admirable and helps me to put a lot of faith in the data and its analysis. The authors tap into the power of the PDF method to explore the effects of a small particle on structure of a solvent.
I believe this application of the PDF method is an important step forward.
Still my major reservation of this really excellent piece of experimentation is the wider context of the surface perturbation on the structure and dynamics of water. As the authors point out this is a time averaged structure over the time of the x-ray measurement. They point to the work of Mamonotov et al. (ref 13 in rebuttal and ref 14 in text of the manuscript) where two clear types of water are identified. Is there any link to the distance from the solvent/particle interface and the perturbation of the structure from that of the bulk? Could the same be said of dynamics?

Our response: We thank the Reviewer for getting back into this broad discussion.
The work by Mamonotov et al. uses quasielastic neutron scattering (QENS). Since neutrons have low flux compared to X-rays, the average measurement times are minutes or hours. The derived dynamics of the hydration layers are in the pico- and nanosecond range, but measurement times also average over way longer time scales in order to collect sufficient statistics.
That said, Mamonotov et al. identified "*three structurally distinct sorbed water layers L_1, L_2, and L_3, where the L_1 species are either associated water molecules or dissociated hydroxyl groups in direct contact with the surface, L_2 water molecules are hydrogen bonded to L_1 and structural oxygen atoms at the surface, and L_3 water molecules are more weakly bound*". L_3 molecules were shown to move fast as they are loosely bound and L_2 water molecules are more strongly bound and slowed down in their dynamics to a nanosecond time-scale.
Since Mamonotov et al. studied different hydroxylated and nonhydroxylated surfaces of rutile (TiO_2) and cassiterite (SnO_2), even within their study, they did not make a generalized answer to the structure and dynamics of the different layers, see the quote "*L_3 molecules on the hydroxylated surface (cassiterite) form a distinct peak at 6 Å, which suggests ordering of water molecules that differs considerably from bulk and the nonhydroxylated surface of rutile.*" Their own comparison between QENS and MD results in Figure 12 connects the different dynamics from QENS with the distance from the metal oxide surface. This, in general, agrees well with our observations with having a strongly adsorbed water layer (their L_1 and our first sharp peaks between $1 - 2.5$ Å) and more loosely bound hydration layers (their L_2 and L_3 and our extended oscillation).
Mamonotov et al. states right in the introduction, that due to differences in bulk dielectric constants, electronegativities and lattice spacings, an easy comparison even of isostructural oxides is not trivial. In our manuscript, we explicitly only compared our dd-PDFs to theoretical findings on magnetite surfaces, as hematite produces different structural fingerprints.

To summarize, metal oxides in general show hydration layers, which have varying properties with the distance from the solvent/particle interface, and which are different from the bulk solvent. The hydration layers possess a substructure, which consists of most commonly at least two different layers – one strongly adsorbed and one more loosely bound layer. The number of the latter strongly varies dependent on the metal oxide / solvent combination. The differences of those hydration layers, or respectively types of water, are reflected in both dynamics and structure. However, it is the metal oxide and its exposed facets which can lead to large variations in the observed dynamics and structure.

Our alteration: In order to further address this general issue, we added to the manuscript right after the quote of Mamonotov et al.:
==“The hydration layers at metal oxide surfaces differ, in general, from the bulk water properties and show modified dynamics and structure, typically varying within the individual layers.”==

I note that the two different methods for examining the solution structure of the particles in the supplementary material, DLS and SAXS, one which are dependant on the dynamics or Brownian motion of the whole particle and electron density variations within the solution give slightly different values of the radius. Is the fact the DLS radius is slightly larger indicative of a strongly perturbed layer of water which contributes to the hydrodynamic radius of the particle?

Our response: We thank the reviewer for this observation.
SAXS provides the electron density variation ($I \sim \Delta\rho^2 V_P^2$). Since our organic molecules are small and light scatterers with much accessible particle surface, a spherical shape model was applied to fit the particle size in SAXS. SAXS gives a diameter of 6 ± 1.8 nm for the ligand cysteamine.
DLS provides the hydrodynamic (or Stokes) diameter, which is that of a sphere that has the same translational diffusion coefficient of Brownian motion as the particle being measured. The size estimation also assumes spherical shape. For the same ligand the SAXS measurement was carried out, i.e. cysteamine, the number-weighted average DLS radius of three measurements with a Particle Analyzer Litesizer 500 was 7.0 ± 0.2 nm. There is a variety of literature, which in general correlates enhanced DLS diameters with water layers and the wording ranges widely, such as structured water, water layer, ordered water or hydration layers. Since we know (see introduction) from various techniques that there are sub-layers to the overall hydration shell, it is hard to tell which of those different layers truly contribute to an enlarged hydrodynamic diameter in DLS. Our dd-PDFs extend over up to 15 Å, but the DLS diameters are not larger than the dry diameter (projected area) observed in TEM by 3 nm (see Supporting Table 1). Therefore, only part of the layers which we see with PDF can contribute to the DLS diameter. But it is for sure true to say that for strongly adsorbed water molecules, there will likely be an effect on the hydrodynamic diameter in DLS.

Our alteration: In order to make it clear which different diameters are in fact measured, we included this information in the manuscript in the Results section with the subheading "Synthesis and characterization of the IONPs":
"IONP sizes were determined using transmission electron microscopy (TEM) (==diameter from== ==projected area==, Supplementary Figure 3), dynamic light scattering (==hydrodynamic diameter==, Supplementary Table 1; Supplementary Figure 4) and SAXS (==particle size based on X-ray scattering contrasts==, Supplementary Figure 4)."

Further we realized, that we should make clear where the average value and standard deviation for DLS diameters in Supplementary Table 1 come from. Therefore, we added a phrase to the Methods subsection Dynamic Light Scattering (DLS) and zeta potential:

==For each method three measurements were conducted and the average values with the standard deviation were calculated.==

A small point is the DLS results would be best presented as the fit to the intensity auto-correlation function. This is a better indication of the tight dispersity in particle size.

Our response: We thank the reviewer for this suggestion. We are happy to additionally provide the intensity auto-correlation function with its fit for the same sample of which SAXS data was acquired.

Our alteration: We changed Supplementary Figure 4. We now supply two panels. Panel **a** shows the SAXS data of cysteamine-capped IONPs as before and panel **b** depicts the intensity auto-correlation function of the same sample with its fit and the number-weighted size distribution in an inset.

Supplementary Figure 4 | Exemplary SAXS and DLS data of cysteamine-capped iron oxide nanoparticle dispersion. a, The Figure shows an exemplary SAXS measurement of cysteamine-capped IONPs of about 7 nm in diameter. The fit for a sphere with diameter 6 ± 1.8 nm describes the SAXS data very well. **b,** The intensity auto-correlation function of the same sample measured with a Particle Analyzer Lite 500 and the provided fit are shown. The number-weighted average size of this measurement is 7.1 nm (average of three measurements 7.0 ± 0.2). The number-weighted average size distribution is depicted in the inset.

Reviewer Two:

The revised manuscript by Thoma, et al. is notably improved, in particular by the addition of several more figures into the supplementary data. The manuscript itself is only very slightly modified, but the inclusion of additional references and several points of clarification, in addition to the new supplemental data, make the paper stronger in its arguments. The additional supplemental data addresses my earlier concerns about the challenges in measuring such small signals, and including the data allows the reader to make his or her own evaluation of the analysis.
One trivial comment: on line 264 in the methods section, the authors write "silicium" instead of "silicon."

Our alteration: We thank the Reviewer, that he found that missing translation from German to English. Of course we corrected it.