



Experiment title: Structure and transport anomalies in soft thiolated gold nanocolloids

Experiment number:
SC-4439

Beamline: ID10	Date of experiment: from: 02.02.17 to: 07.02.17	Date of report: 05.03.18
Shifts: 15	Local contact(s): Federico Zontone	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Avni Jain*¹, Felix Lehmkuehler*¹, Florian Schulz*², Irina Lokteva*¹, Lara Frenzel*^{1,2}, Gerhard Gruebel^{1,2}

1: Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

2: Institut für Physikalische Chemie, Universität Hamburg, Hamburg, Germany

Report:

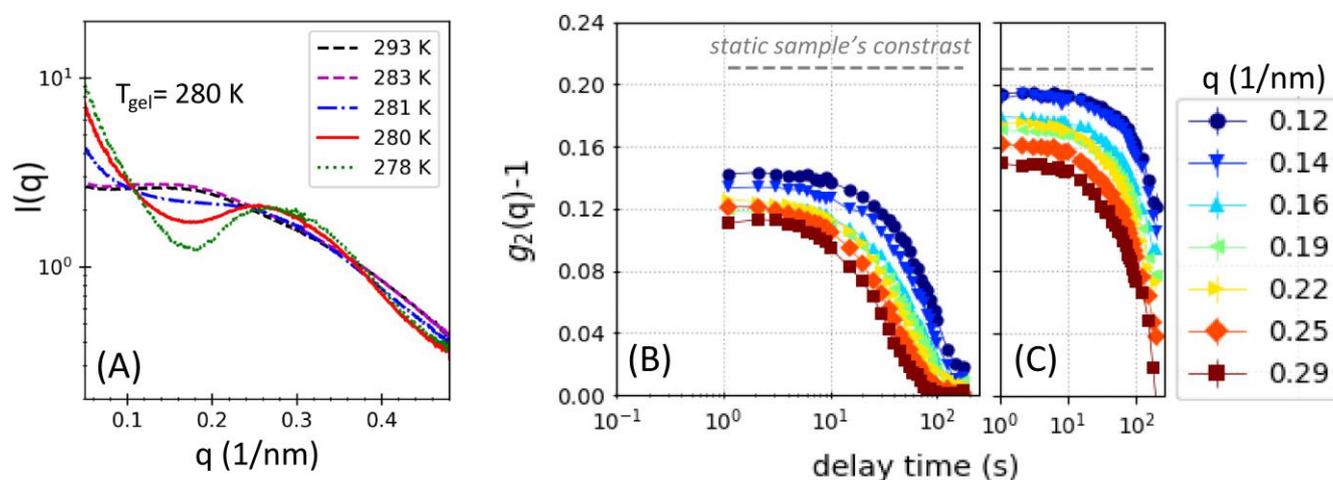
It has been predicted via simulations that for particles with non-directional, core-softened repulsive interactions, particle correlations decrease and mobility increases with increasing particle concentration, contrary to the behaviour of hard spheres.[1] Such core-softened potentials were initially modeled to reliably quantify the entropic repulsions between self-avoiding polymer chains in a good solvent.[2] Recently, an experimental realization of such anomalous transport and structural trends in colloidal suspensions was demonstrated for polyethylene glycol (PEG)-grafted silica nanoparticles (>10 nm silica core diameter) suspended in PEG.[3] In this experiment, we proposed to study the temperature-dependent structure and dynamics of alkyl thiol-grafted gold nanoparticles (AuNPs) and PEG-grafted AuNPs, of varying degree of softness, solvated in a polymeric fluid host in the SAXS geometry using XPCS. We hypothesized to observe similar anomalous dynamics as in [3]. Their degree of softness, generally measured by the ratio of shell thickness to core radius at dilute concentrations [4] is easily tunable by choice of the AuNP core size and the stabilizing ligand.

The experiment was performed at ID10. We used the MAXIPIX 2x2 detector with a sample detector distance of ~ 5100 mm. In the first two shifts, we measured capillaries filled with the following samples, 2 nm diameter AuNP grafted with (a) octanethiol, (b) hexadecanethiol, (c) octadecanethiol. The preliminary results showed dynamics of these samples to be correlated with the attenuation used, clearly implying radiation damage. Due to the fact that we could not disentangle the dynamics due to beam damage or due to the sample itself, we *did not further pursue the thiol-grafted gold nanoparticles*.

We then measured the dynamics of PEG-grafted gold nanoparticle samples at various temperatures, and observed highly interesting heterogenous dynamics. However, we did not

observe any dynamic anomaly based on the softness of the nanoparticles. The effectively-smaller sized less soft nanoparticles were faster than the larger-sized softer particles. Our experiment can be summarized as:

1. We measured two types of sample systems at 3 different concentrations: 12 nm diameter Au-particles stabilized with a 12 nm PEG shell (12-12) (degree of softness ~ 1) and the other with a 8 nm PEG shell (12-8) (degree of softness ~ 0.67), in a 70-30 vol/vol glycerol water mixture. We saw the sample system aggregate into a gel-like phase at colder temperatures ($T^* \sim 280\text{K}$ for the larger 12-12 nanoparticles and $T^* \sim 278\text{K}$ for the smaller 12-8 NPs). We measured XPCS dynamics and SAXS at T^* and also at slightly lower than T^* (T^*-2) at different waiting times. Some key results are that we clearly see q -dependent lack of contrast in the intensity autocorrelation g_2 functions and a difference in the dynamics at different waiting times for a sample. Also, the 12-8 sample was ~ 2 orders of magnitude faster than the 12-12 sample. The q -dependent lack of contrast is consistent with features of colloidal fractal gels [5] and also demonstrate that the g_2 would decay partially at timescales $< 1\text{s}$ for the 12-12 sample.



(A) Intensities of the (12-12) colloidal gel at different temperatures, where agglomeration occurs at $T=280\text{K}$; (B) Intensity autocorrelation functions, $g_2(q)-1$, at wait time = 600s after set temperature $T=280\text{K}$ is reached; (C) $g_2(q)-1$ at wait time = 3000s. The contrast of the static sample = 0.21 (grey dashed line). Note the lack of contrast at short delay times varies as a function of the lengthscale ($1/q$) and wait times, clearly implying the existence of partial decay process(es) $< 1\text{s}$ and non-ergodic behaviour.

2. We also measured the PEG-Au NPs in a 90-10 vol/vol PEG300/water mixture. Quite unexpectedly, we observed that these systems gelate as well. However, these samples were much more sensitive to beam damage.

Further data analysis of the XPCS results and modeling of the g_2 functions is ongoing.

As these measurements were being done in absolute time and we had to carefully track the time once the target temperature was reached. Hence, the occurrence of beam dumps really hampered the measurement. It also took us one whole shift per sample to experiment with the exposure time and attenuation parameters to fully ensure the change in dynamics was not due to radiation damage. The temperature switch could only be controlled from inside the chamber, further increasing the time of measurement.

References:

- [1] W.P. Krekelberg et al. *Phys. Rev. E* **79**, 031203 (2009); L. Berthier et al. *Phys. Rev. E*. **82**, 060501 (2010); M.J. Pond et al. *Soft Matter* **7**, 9859 (2011)
- [2] C.N. Likos et al. *Phys. Rep.* **348**, 267 (2001)
- [3] S. Srivastava et al. *Phys. Rev. Lett* **110** 148302 (2013)
- [4] B. Korgel et al. *Phys. Rev. B* **59**, 14191 (1999); BW Goodfellow et al. *ACS Nano* **5**, 2419 (2011)
- [5] H Guo et al. *J. Chem. Phys.* **135**, 154903 (2011);