1 Samples: characterization and supercrystal structure

The nanoparticles used (NPs) are gold nanoparticles grafted with thiol ligands. The gold core diameter and its polydispersity have been measured using Small Angle X-ray Scattering (SAXS) on dilute suspensions (less than 1wt% in oil). The NP polydispersity has been determined using a Schulz-Zimm distribution. The fits were performed using the NIST softwares: "Reduction and Analysis of SANS and USANS Data using Igor Pro", Kline, S. R. J Appl. Cryst. 39(6), 895 (2006).

The NPs have been dispersed in a volatile solvent (toluene or cyclohexane) at relatively large weight fraction (typically 10wt%) to determine the structure of NPs supercrystals. Then the suspensions have been poured in capillaries, either x-ray capillaries (1mm diameter, WJM Glas®) or in flat glass capillaries (VitroCom® 0.1 mm x2 mm). The capillaries have been sealed at one end and centrifugated. They were kept vertical at room temperature for several weeks in order to induce a slow evaporation of the solvent. For each batch (see Table I), several capillaries have been prepared and scanned in the X-ray beam at different vertical positions.

| Batch | Core Diameter (nm) | Polydispersity % | Ligand | Structure | a         | Nb |
|-------|--------------------|------------------|--------|-----------|-----------|----|
| CG62  | 2.10               | 11%              | C6-thiol | C14       | 5.88 - 5.90 | 6  |
| AL293 | 2.12               | 15%              | C6-thiol | C14       | 5.83 - 5.83 | 2  |
| CG57  | 2.3                | 15%              | C6-thiol | C14       | 5.99 - 6.07 | 3  |
| AL253 | 2.71               | 17%              | C6-thiol | C14       | 6.91 – 7.01 | 5  |
| AL67  | 2.44               | 16%              | C7-thiol | C14       | 7.08       | 3  |
| AL66  | 1.98               | 20%              | C8-thiol | C14       | 6.48       | 3  |
| AL291 | 2.28               | 16%              | C9-thiol | C14       | 6.47       | 3  |
| AL290 | 2.1                | 13%              | C10-thiol | BCC       | 4.12- 4.15 | 6  |
| CG21  | 3.39               | 12%              | C10-thiol | C14       | 8.64       | 6  |
| CG20  | 3.93               | 10%              | C10-thiol | C14       | 9.55       | 3  |
| CG49  | 4.38               | 10%              | C10-thiol | C14       | 10.36      | 5  |
| Batch | Core Diameter (nm) | Polydispersity % | Ligand   | Structure | a     | Nb |
|-------|-------------------|------------------|----------|-----------|-------|----|
| AL315 | 1.99              | 15%              | C12-thiol| BCC       | 4.29  | 2  |
| AL313 | 2.01              | 13%              | C12-thiol| BCC       | 4.27  | 2  |
| CG59  | 2.1               | 11%              | C12-thiol| BCC       | 4.24  | 2  |
| AL201 | 2.17              | 12%              | C12-thiol| BCC       | 4.36-4.40 | 2 |
| AL240 | 2.19              | 12%              | C12-thiol| BCC       | 4.42-4.39 | 2 |
| AL113 | 2.3               | 12%              | C12-thiol| BCC       | 4.49  | 2  |
| AL310 | 3.45              | 10%              | C12-thiol| C14       | 9.3   | 4  |
| CG39  | 3.48              | 9%               | C12-thiol| FCC       | 8.06-8.11 | 5 |
| CG54  | 3.7               | 13%              | C12-thiol| C14       | 9.87  | 4  |
| CG41  | 3.96              | 9%               | C12-thiol| C14       | 9.94  | 5  |
| CG51  | 3.98              | 14%              | C12-thiol| C14       | 10.36-10.39 | 4 |
| AL279 | 4.25              | 12%              | C12-thiol| C14       | 10.67 |     |
| CG50  | 4.4               | 12%              | C12-thiol| C14       | 10.51 | 5  |
| AL256 | 4.82              | 9%               | C12-thiol| FCC       | 9.67  | 1  |
| CG61  | 2.1               | 12%              | C14-thiol| BCC       | 4.33  | 4  |
| CG58  | 2.2               | 9%               | C14-thiol| BCC       | 4.57  | 4  |
| CG55  | 3.6               | 10%              | C14-thiol| C14       | 9.94  | 4  |
| CG52  | 3.92              | 10%              | C14-thiol| C14       | 10.67 | 4  |
| CG47  | 4.7               | 10%              | C14-thiol| C14       | 11.16 | 5  |
| AL256 | 4.82              | 10%              | C12-thiol| FCC       | 9.67  |     |
| CG42  | 5.1               | 10%              | C14-thiol| FCC       | 11.57 | 6  |

**Table 1** Table of samples: batch name, core diameter in nm, ligand, observed structure, cell parameter $a$ in nm, number of samples Nb.
2 Geometry and crystallography

For a FCC structure, the cell is cubic (parameter $a$). The space group is $Fm\bar{3}m$. The first diffraction peak corresponds to $q_{1_{FCC}} = q_{111} = \sqrt{3} \times 2\pi / a$. The distance between neighboring particles is $a/\sqrt{2} = \frac{2\pi}{q_{1_{FCC}}} \sqrt{3}/2$. There are 4 particles per cubic cell and therefore the mean volume per particle is $a^3/4$. The different diffraction peaks are given in Table 3.

For a BCC structure, the cell is cubic (parameter $a$). The space group is $Im\bar{3}m$. The first diffraction peak corresponds to $q_{1_{BCC}} = q_{110} = \sqrt{2} 2\pi / a$. The distance between neighboring particles is $a\sqrt{3}/2 = \frac{2\pi}{q_{1_{BCC}}} \sqrt{3}/2$. There are 2 particles per cubic cell and therefore the mean volume per particle is $a^3/2$. The different diffraction
peaks are given in Table 4. For FCC and BCC structures, all the sites are equivalent and the structure factor is the same for all Bragg peaks.

For a A15 structure, the cell is cubic (parameter $a$). The space group is $Pm\bar{3}n$. The first diffraction peak corresponds to $q_{A15} = q_{200} = 2 \times 2\pi / a$. The smallest distance between neighboring particles is $a/2 = \frac{2\pi}{q_{A15}}$. There are 8 particles per cubic cell and therefore the mean volume per particle is $a^3/8$. The different diffraction peaks are given in Table 5. Since all the sites are not equivalent with two different sites, each of them contribute differently to the structure factor (the diffraction peaks have not all the same intensity). However, in Table 5 we consider that all sites are occupied by only one type on NP.

For a C14 structure, the cell is hexagonal (parameters $a$ and $c = \sqrt{3/2} a$). The space group is $P6_3/mmc$. The first diffraction peak corresponds to $q_{C14} = q_{100} = 2 \sqrt{3} \times 2\pi / a$. The smallest distance between neighboring particles is $a/2 = \frac{1}{\sqrt{3}} q_{C14}$. There are 12 particles per cubic cell (2+4+6) and therefore the mean volume per particle is $\sqrt{2} a^3/12$. The different diffraction peaks are given in Table 6. Since all the sites are not equivalent, the structure factor is not the same for all Bragg peaks. As in the case of the A15 structure, we consider in Table 6 that all sites are occupied by only one type of NP.

Other structures have also been observed in soft matter like the $\sigma$ phase and the C15 phase. The C15 phase is a cubic phase; it is the FCC version of the hexagonal C14 phase. The cell is cubic (face centered). There are 4+4*4=20 particles in the cubic cell. The space group is $Fd\bar{3}m$. The first diffraction peak corresponds to $q_{1FCC} = q_{111} = \sqrt{3} \times 2\pi / a$. The smallest distance between the first neighbor is $d = a \sqrt{2} / 2 = \sqrt{6} \times 2\pi / q_{C15}$.

The $\sigma$ phase is tetragonal with space group $P4_2/mmm$. The quadratic cell contains 30 nanoparticles distributed on 5 different crystallographic sites. The ratio $c/a$ is close to 0.529. The first diffraction peak corresponds to $q_{1\sigma} = q_{110} = \sqrt{2} \times 2\pi / a$. The first neighbouring distance is $d = 0.266a = 0.266 \times \sqrt{2} \times 2\pi / q_{1\sigma}$.

| Structure | Cell Shape | Number of Sites | First Peak Location | Neighboring Distance $d$ |
|-----------|------------|-----------------|---------------------|--------------------------|
| FCC       | cubic      | 4               | $q_{111} = \sqrt{3} \times 2\pi / a$ | $a/\sqrt{2}$             |
| BCC       | cubic      | 2               | $q_{110} = 2 \times 2\pi / a$ | $a\sqrt{3}/2$            |
| A15       | cubic      | 8(2+6)          | $q_{200} = 2 \times 2\pi / a$ | $a/2$                    |
| C14       | hexagonal  | 12 (2+4+6)      | $q_{100} = \frac{2}{\sqrt{3}} \times 2\pi / a$ | $a/2$                    |
| C15       | cubic      | 20(4+16)        | $q_{111} = \sqrt{3} \times 2\pi / a$ | $a \sqrt{2}/4$          |

Table 2: Comparison between the different structures.
| hkl  | $h^2 + k^2 + l^2$ | $q/q_1$ | mult |
|------|-----------------|---------|------|
| 111  | 3               | 1       | 8    |
| 200  | 4               | 1.154   | 6    |
| 220  | 8               | 1.632   | 12   |
| 311  | 11              | 1.915   | 24   |
| 222  | 12              | 2       | 8    |
| 400  | 16              | 2.31    | 6    |
| 331  | 19              | 2.51    | 24   |
| 420  | 20              | 2.58    | 16   |
| 422  | 24              | 2.83    | 24   |
| 500  | 25              | 2.89    | 6    |
| 333  | 25              | 3       | 8    |
| 511  | 27              | 3       | 24   |
| 440  | 32              | 3.26    | 12   |
| 531  | 35              | 3.42    | 48   |

Table 3: Crystallographic data for the FCC phase.

| hkl  | $h^2 + k^2 + l^2$ | $q/q_1$ | mult |
|------|-----------------|---------|------|
| 110  | 2               | 1       | 12   |
| 200  | 4               | 1.41    | 6    |
| 211  | 6               | 1.73    | 24   |
| 220  | 8               | 2       | 12   |
| 310  | 10              | 2.24    | 24   |
| 321  | 14              | 2.65    | 48   |
| 400  | 16              | 2.83    | 6    |
| 420  | 20              | 3.16    | 24   |
| 422  | 24              | 3.46    | 24   |
| 510  | 26              | 3.61    | 24   |
| 512  | 30              | 3.87    | 48   |
| 440  | 32              | 4       | 12   |

Table 4: Crystallographic data for the BCC phase.

| hkl  | $h^2 + k^2 + l^2$ | $q/q_1$ | Int  | mult |
|------|-----------------|---------|------|------|
| 200  | 4               | 1       | 16   | 6    |
| 210  | 5               | 1.12    | 16   | 24   |
| 211  | 6               | 1.22    | 16   | 24   |
| 222  | 12              | 1.73    | 16   | 8    |
| 320  | 13              | 1.80    | 16   | 24   |
| 321  | 14              | 1.87    | 16   | 48   |
| 400  | 16              | 2       | 64   | 6    |
| 420  | 20              | 2.24    | 16   | 24   |
| 421  | 21              | 2.29    | 16   | 48   |
| 332  | 22              | 2.35    | 16   | 24   |

Table 5: Crystallographic data for the A15 phase with only one type of NP on all the sites.
| hkl | $q/q_1$ | Int | mult |
|-----|---------|-----|------|
| 100 | 1       | 0.97| 6    |
| 002 | 1.061   | 1.33| 2    |
| 101 | 1.137   | 0.43| 12   |
| 102 | 1.458   | 0.17| 12   |
| 110 | 1.732   | 16  | 6    |
| 103 | 1.879   | 24.28|12  |
| 200 | 2       | 9   | 6    |
| 112 | 2.031   | 46.86|12 |
| 201 | 2.069   | 42.4| 12   |
| 004 | 2.121   | 64.8| 2    |
| 202 | 2.264   | 12.79|12 |
| 104 | 2.345   | 8.76| 12   |
| 203 | 2.556   | 4.03| 12   |
| 211 | 2.698   | 0.159|24 |
| 114 | 2.738   | 0.0025|24 |
| 105 | 2.834   | 2.19| 12   |
| 212 | 2.85    | 0.201|24 |
| 204 | 2.915   | 1.05| 12   |
| 123 | 3.087   | 24.04|24 |
| 205 | 3.321   | 70.8| 12   |
| 214 | 3.391   | 9.02| 24   |

**Table 6**: Crystallographic data for the C14 phase with only one type of NP on all the sites.

| hkl | $q/q_1$ | Int | mult |
|-----|---------|-----|------|
| 111 | 1       | 5.49| 8    |
| 220 | 1.63    | 64  | 12   |
| 311 | 1.91    | 186 | 24   |
| 222 | 2       | 256 | 8    |
| 400 | 2.31    | 64  | 6    |
| 331 | 2.52    | 5.49| 24   |
| 422 | 2.83    | 64  | 24   |
| 333 | 3       | 186 | 8    |
| 440 | 3.27    | 576 | 12   |
| 531 | 3.42    | 5.49| 48   |

**Table 7**: Crystallographic data for the C15 phase with only one type of NP on all the sites.
| hkl | $q/q_1$ | Int   | mult |
|-----|---------|-------|------|
| 110 | 1       | 0.043 | 4    |
| 200 | 1.414   | 0.0115| 4    |
| 101 | 1.512   | 0.967 | 8    |
| 210 | 1.5811  | 0.0098| 8    |
| 111 | 1.669   | 1.1127| 8    |
| 220 | 2       | 0.061 | 4    |
| 211 | 2.0704  | 0.0795| 16   |
| 310 | 2.236   | 1.78  | 8    |
| 221 | 2.406   | 1.198 | 8    |
| 301 | 2.5073  | 1.347 | 8    |
| 320 | 2.5495  | 0.311 | 8    |
| 311 | 2.6051  | 5     | 16   |
| 002 | 2.6734  | 196   | 2    |
| 400 | 2.8284  | 0.64  | 4    |
| 112 | 2.8543  | 6.83  | 8    |
| 321 | 2.8787  | 0.973 | 16   |
| 410 | 2.9155  | 216.4 | 8    |
| 330 | 3       | 234.4 | 4    |
| 202 | 3.0244  | 104.8 | 8    |
| 212 | 3.1059  | 124.5 | 16   |
| 420 | 3.1623  | 2.05  | 8    |
| 411 | 3.2073  | 202   | 16   |
| 331 | 3.2073  | 196   | 8    |
| 222 | 3.3387  | 41    | 8    |

*Table 8*: Crystallographic data for the $\sigma$ phase with only one type of NP on all the sites.
3 Experimental structure factors

The structure factor $S(q)$ can be determined experimentally using: 

$$S(q) = \alpha (I(q) - I_{bgd}) / FF(q)$$

where $I(q)$ is the measured intensity, $I_{bgd}$ is the background intensity assumed to be constant, $FF(q)$ is the form factor of the NPs and $\alpha$ is a constant scale parameter that fix $S(q) = 1$ when $q$ is large. The graph $S(q)$ as a function of $q$ reveals the diffraction peaks more clearly.

![Graph of $S(q)$ as a function of $q$](image)

**Figure 2**: Experimental structure factor, BCC phase.

![Graph of $S(q)$ as a function of $q$](image)

**Figure 3**: Experimental structure factor, interpreted as due to a FCC phase.
4 Model of the SAXS intensity scattered by supercrystals.

The intensity scattered by supercrystals is characterized by diffraction peaks depending on the structure, as described in a previous section. If there are several supercrystals with random orientation in a sample, these peaks appear as uniform circles at a given \( q \) position (\( I_{\text{struct}} \)) on the two-dimensional SAXS image. If the orientation of the supercrystals is not randomly distributed, the SAXS image exhibits spots located on these circles. The scattered intensity can be represented using a radial integration \( I(q) \) at a given \( q \) value. The scattered intensity is modulated by the form factor of the nanoparticles \( FF(q) \) as measured on dilute suspensions and a Debye-Waller attenuation factor taking into account thermal fluctuations.

Experimentally three other contributions have to be added to describe more properly the scattered intensity. At low \( q \), the intensity increase can be explained by the presence of supercrystals with a small size, giving a contribution that behaves as \( I_1(q) \approx 1/q^4 \), corresponding to the Porod scattering by their external surface. The other contribution is a diffuse peak whose maximum is located in the \( q \) region where the diffraction peaks are intense. It can be interpreted as due to amorphous zones without any crystalline order between the nanoparticles. This contribution can be modelled using the structure factor \( S_{HSS}(q) \) of a dense hard spheres assembly (Percus-Yevick analytical expression) characterized by the hard sphere radius \( R_{HSS} \) and their volume fraction close to 50%. The last contribution is a background \( I_{bg} \) that has been taken as constant, independent of \( q \). The peak intensities is modulated by a Debye-Waller factor in order to take into account the thermal disorder.

A model of the total intensity is thus

\[
I_{\text{mod}}(q) = I_{\text{struct}} * FF(q) * \exp(-\delta^2 q^2) + S_{HSS}(q) * FF(q) + I_1(q) + I_{bg}
\]  

Two examples are given in the following graphs where the contribution of \( I_1(q) \) and \( S_{HSS}(q) * FF(q) \) are shown by dotted lines.
Figure 5: Modelization of the intensity $I(q)$ scattered by an assembly of C14 supercrystals with the sum of the four contributions.

Figure 6: Radial intensity $I(q)$ in arbitrary unit as a function of $q$ in Å$^{-1}$ for the CG50 batch (Gold core diameter 4.4 nm, ligand C12-thiol). Comparison with the intensity expected for a C15 phase: the peaks that cannot be indexed by a C14 structure cannot be indexed by a C15 structure.

5 Size ratio $e/L$.

The ligand thickness in-between two neighboring gold cores is referred by $e$ and can be compared to $L$, the ligand full extended length (see the main text). $e$ is obtained from $d$, the smallest distance between two NPs in a structure (see Table 2, by subtracting to it the gold core diameter $D$: $e = d - D$. In Table 9, values of the ratio $e/L$ are given for different samples and different structures for increasing values of $D$. When several cell parameters have been measured for the same batch, the error on $e$ is given between brackets. Values of the volume fraction occupied by the gold cores are also given in Table 9.

| Batch | $D$ in Å | ligand-thiol | $L/D$ | $L/R$ | phase | $e/L$ mean value | Gold core vol. fract. |
|-------|---------|--------------|-------|-------|-------|-----------------|---------------------|
| AL66  | 19.8    | C8           | 0.61  | 1.22  | C14   | 1.05            | 13%                 |
| AL315 | 19.9    | C12          | 0.85  | 1.71  | BCC   | 1               | 11%                 |
| Material | e/L | e/C | l/L | Structure | Volume Fraction |
|----------|-----|-----|-----|-----------|-----------------|
| AL313    | 20.1| 0.85| 1.69| BCC       | 0.99 11%        |
| CG59     | 20.9| 0.82| 1.63| BCC       | 0.93 12.5%      |
| CG62     | 21  | 0.43| 0.86| C14       | 0.93 20%        |
| AL290    | 21  | 0.67| 1.33| BCC       | 1 14%           |
| CG61     | 21  | 0.90| 1.81| BCC       | 0.87 12%        |
| AL293    | 21.2| 0.42| 0.85| C14       | 0.91 21%        |
| AL201    | 21.7| 0.78| 1.57| BCC       | 0.95 13%        |
| AL240    | 21.9| 0.78| 1.55| BCC       | 0.96 13%        |
| CG58     | 22  | 0.86| 1.73| BCC       | 0.92 12%        |
| AL291    | 22.8| 0.57| 1.14| C14       | 0.73 20%        |
| CG57     | 23  | 0.39| 0.78| C14       | 0.80 25%        |
| AL113    | 23  | 0.74| 1.48| BCC       | 0.93 14%        |
| AL67     | 24.4| 0.39| 0.79| C14       | 1.1 18%         |
| AL253    | 27.1| 0.33| 0.66| C14       | 0.88 26%        |
|          |     |     |     | FCC       | 1.9 17%         |
| CG21     | 33.9| 0.41| 0.83| C14       | 0.66 27%        |
| AL310    | 34.5| 0.49| 0.99| C14       | 0.70 23%        |
|          |     |     |     | FCC       | 1.3 17%         |
| CG39     | 34.8| 0.49| 0.99| FCC       | 1.32 17%        |
|          |     |     |     | C14       | 0.7 24%         |
| CG54     | 37  | 0.46| 0.92| C14       | 0.73 23%        |
| CG52     | 39.2| 0.48| 0.97| C14       | 0.74 22%        |
| CG20     | 39.3| 0.36| 0.71| C14       | 0.6 31%         |
| CG41     | 39.6| 0.43| 0.86| C14       | 0.61 28%        |
| CG51     | 39.8| 0.43| 0.85| C14       | 0.71 25%        |
| AL279    | 42.5| 0.4 | 0.8 | FCC       | 1.65 16%        |
|          |     |     |     | C14       | 0.64 28%        |
| CG49     | 43.8| 0.32| 0.64| C14       | 0.57 34%        |
| CG50     | 44  | 0.39| 0.77| C14       | 0.51 33%        |
| CG47     | 47  | 0.4 | 0.81| C14       | 0.46 33%        |
| AL256    | 48.2| 0.35| 0.71| FCC       | 1.2 26%         |
| CG42     | 51  | 0.37| 0.75| FCC       | 0.95 30%        |

**Table 9**: Size ratio \( e/L \) and gold core volume fraction.