Determination of the local density of polydisperse nanoparticle assemblies

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### ELECTRONIC SUPPLEMENTARY INFORMATION

1. **Check for the absence of finite-size effects**

We have performed calculations to show that there is no problem with finite size in the ‘infinite’ systems (first Results section of the manuscript). In Fig. S1, one can see an example of the absence of finite-size effects, comparing the experimental structure factor (20%, polydispersity 15%) of systems with 1000 and 8000 spheres. The smaller system is thus twice as small in any given direction, and $q_0$ is thus twice as big – this effect is also visible in Figure 1a. The agreement shows that there is no noticeable finite size effect, in spite of the very small system size.

![Log-log plot of the experimental structure factor S(q) as a function of wave vector q for an “infinite” HS ensemble (R₀ = 10 nm, σ = 15%, volume fraction 20%v) with 1000 and 8000 spheres.](image)

**Fig. S1** Log-log plot of the experimental structure factor S(q) as a function of wave vector q for an “infinite” HS ensemble ($R₀ = 10$ nm, $σ = 15\%$, volume fraction 20%v) with 1000 and 8000 spheres.
2. Additional simulated structure factors

Two series of simulated structure factors as a function of polydispersity $\sigma$ are shown in Fig. S2 for additional volume fractions, $\kappa$.

**Fig. S2** Log-log plot of the experimental structure factor $S(q)$ as a function of wave vector $q$ for an “infinite” HS ensemble ($R_0 = 10$ nm) with polydispersity $\sigma$ ranging from 0 to 45% as given in the legend. (a) $\kappa = 10\%$, (b) $\kappa = 30\%$.

Two series of simulated structure factors as a function of volume fraction $\kappa$ are shown in Fig. S3 for two polydispersity values, $\sigma = 15\%$ and 30\%.

**Fig. S3** Log-log plot of the experimental structure factor $S(q)$ as a function of wave vector $q$ for an “infinite” HS ensemble ($R_0 = 10$ nm) with volume fraction $\kappa$ ranging from 0 to 40% as given in the legend. (a) $\sigma = 15\%$, (b) $\sigma = 30\%$. 
3. Variation of the aggregate shape

The depth of the correlation hole is estimated using well-defined aggregates contained in a sphere, with the side effect of form factor oscillations. Due to the oscillations, there is some error bar on the estimation of the depth of the correlation hole – given by the second local minimum –, which has been illustrated by a black line in Figure 3, as a guide to the eye. We have performed calculations with different shapes (cubes, spheres, cylinders) of aggregates, providing an idea of the robustness of our estimation. The results are shown in Fig. S4.

![Fig. S4 Log-log plot of structure factors S(q) as a function of wave vector q for finite HS systems (R_0 = 10 nm, σ = 15%, κ = 20%, N_agg = 200) with different geometries as indicated in the legend.](image)

4. Variation of the spherical HS system size

We have checked that the mapping procedure can also be applied to small aggregates by progressively reducing the size of the spherical subset in the simulation box. For small aggregates, one may wonder by how much the correlation hole analysis is influenced by the low-q upturn associated with the aggregate size. We have therefore performed a series of simulations of different NP numbers in the subset, from N_agg = 25 to 950, mimicking changes in aggregate size. All other parameters were kept constant (R_0 = 10 nm, σ = 15%, κ = 20%). The resulting S(q) are shown in Fig. S5. The global minimum of S(q) is seen to be robust.
5. Aggregate construction algorithm

Aggregates of different density have been simulated by imposing different numbers of direct neighbors during aggregate construction. The starting point is the algorithm used in ref. 1 (see A1 below), where \( N_{agg} \) polydisperse spheres obeying the log-normal size distribution \((R_0 = 10 \text{ nm}, \sigma = 15\%)\) are successively placed in contact, starting with a first particle located at the origin, in a random direction. In the model calculations in this paper, \( N_{agg} \) has been set to 200. Each new particle is placed in contact with any of the previously placed ones, chosen according to the rules below. Both the coordination number (i.e., the number of neighbors placed in exact contact) and the excluded volume (i.e., no collisions) are then checked, giving the following possible construction algorithms of different densities:

**A1:** The particle is placed next to a randomly chosen particle. The coordination number is left free, only the excluded volume is checked. In case of collision, a new position of the particle – including the random choice of its neighbor – is tried. This gives the open, low-density structures as shown in Fig. 7.

**A2:** The particle is placed next to a randomly chosen particle (without any constraint on coordination), but in case of collision, its position around that particle is (randomly) optimized to fit in the additional particle. This increases the local density.

**A3:** As with A2, but with control of the maximum allowed coordination number \((C_{max})\) of each particle. Particles can only be placed next to particles not reaching the \( C_{max} \). Setting \( C_{max} \) to two allows
simulating self-avoiding chains, whereas denser aggregates are obtained with higher $C_{\text{max}}$ (varying from 3 to 7).

**A4:** As with **A2=A3**, but with a reinforced local density by enforcing positioning next to particles with the highest possible coordination number (the final value staying $\leq C_{\text{max}}$). This is done by establishing a list of coordination numbers, and choosing randomly from the particles with $C = C_{\text{max}} - 1$ (resp. - 2, - 3 if needed). This construction algorithm leads to the densest aggregates, shown in Fig. 8a.

In the main article, comparisons with aggregates made according to the different algorithms (A1-A4) are discussed, with a fixed aggregation number of 200. In order to explore also this parameter, non-spherical aggregates using algorithm A2 have been made containing $N_{\text{agg}} = 50, 100, 200, 400, 800$ particles. As usual, structure factors and local densities $\kappa_{\text{agg}}$ have been determined as averages over hundreds of aggregates. The results are added in Fig. 8b in the main article. The bigger the aggregates, the denser they become, and the less their specific surface and thus number of particles located at the border. This results in an increase in density with size. The structure factors of these aggregates are plotted in Fig. S6.

![Fig. S6](image) Evolution of $S(q)$ of aggregates of different sizes ($N_{\text{agg}} = 50$ to 800, all A2). Inset: 3D snapshot of aggregates with 50 and 800 particles (polydispersity is not graphically represented).

6. Use of the unified scattering law proposed by Beaucage

In Fig. S7, we have applied a two-level model with and without correlations $^2$ to our data in Figure 7a. The first level is defined by the nanoparticle (1: $R_0 = 10$ nm, $\sigma = 15\%$) with a radius of gyration $R_{g,1}$
given by \((3/5 <R_1^2>/<R_1^6>)^{0.5} = 9.1\) nm. The second level corresponds to the aggregate with a fractal dimension \(d_f = 2.5\) and a Guinier radius \(R_2 = 104.6\) nm \((R_{g,2} = 81\) nm\), as obtained from the fit. The ratio between the prefactors of both Guinier contributions (dotted lines in Fig. S7) gives the number of particles within the aggregate: \(N_{agg} = I_2/I_1 = 200\). One can see in Fig. S7a that a purely fractal law does not describe the correlation hole. In Fig. S7b, the correlation term with a correlation length of 20 nm and a local density of 15% (packing fraction = 1.2) approaches the experimental curve somewhat in the intermediate q-range. Note that alternative choices of up to 25% (packing fraction = 2.0) are also possible.

**Fig. S7** Description of the scattered intensity of Figure 7a for simulated aggregates of \(N_{agg} = 200\) polydisperse NPs \((R_0 = 10\) nm, \(\sigma = 15\)%\) by a two-level model without (a) and with (b) correlations \((d_f = 2.5,\) correlation length = 20 nm, packing fraction = 1.2) as proposed by Beaucage \(^2\). Dotted lines represent the Guinier contribution of each level.

**References**
