Supporting Information

of

Measurement of the size distribution of multimodal colloidal systems by laser diffraction

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TABLES OF PARAMETERS

Table S1. Experimental parameter for the laser diffraction method.

| Parameter                                      | Value                  |
|------------------------------------------------|------------------------|
| Beam Length (mm)                               | 2.5                    |
| Alignment Type                                 | Automatic              |
| Analysis Model                                 | Verification Latex     |
| Scattering Model                               | Mie                    |
| Is Particle Fraunhofer?                        | No                     |
| Particle Refractive Index                      | 1.59                   |
| Particle Refractive Index Blue                 | 1.6                    |
| Dispersant Refractive Index                    | 1.33                   |
| Laser Power (%)                                | 78.9 - 79.5            |
| Laser Obscuration (%)                          | 1.2 - 13.9             |
| Obscuration Low Limit (%)                      | 0.01 – 2               |
| Obscuration High Limit (%)                     | 5 – 30                 |
| Stirrer Speed Achieved (rpm)                   | 1000 - 3000            |
| Temperature (°C)                               | 21.7 - 24.5            |
| Weighted Residual (%)                          | 0.40 - 17              |
| Residual (%)                                   | 0.38 - 30              |
| Excluded Inner Detectors                       | 0 - 20                 |

Table S2. Experimental parameter for the differential centrifugal sedimentation method.

| Parameter                                      | Value                  |
|------------------------------------------------|------------------------|
| Light source wavelength (nm)                   | 405                    |
| Disc Speed (rpm)                               | 24000                  |
| Calibration Standard Diameter                  | 0.522                  |
| Calibration Standard Density (g/cm³)           | 1.052                  |
| Nominal Particle Density (g/ml)                | 1.052                  |
| Recalculated particle density (g/cm³)          | 1.046 – 1.054          |
| Particle Refractive Index                      | 1.6                    |
| Particle Absorption                            | 0                      |
| Particle Non-sphericity                         | 1                      |
| Fluid Density (g/ml)                           | 1.018                  |
| Fluid Refractive Index                         | 1.34                   |
| Number of Data Points                          | 733 - 2716             |
Table S3. Experimental parameter for the dynamic light scattering method.

| Instrument Type | NanoZS |
|-----------------|--------|
| Laser Wavelength (nm) | 632.8 |
| Measurements | 3 |
| Runs | 11 |
| Run duration (s) | 5 - 10 |
| Solvent Viscosity (cP) | 0.8872 |
| Refractive Index | 1.330 |
| Temperature (°C) | 25 |
| Equilibration time (s) | 120 |
| Mean Count Rate (kcps) | 144 - 410 |
| Attenuation Factor | 0.00138 – 0.0103 |

Table S4. Method for estimation of the uncertainty of the modal diameter of the volume-weighted size distribution

| Sample | Images | Particles measured | Pixel Size (pixels/µm) | Uncertainty due to pixel size (µm/pixel) | SD in measured diameters (µm) | SD - circularitya (µm) | SD - thresholdb (µm) | SD - manual measurementb (µm) | Total uncertainty (µm) |
|--------|--------|---------------------|------------------------|------------------------------------------|-----------------------------|-----------------------|----------------------|--------------------------|-------------------|
| PSM2   | 18     | 1442                | 34.0                   | 0.03                                     | 0.035                       | 0.0078                | 0.024                | -                        | 0.052             |
| PSM21  | 20     | 1653                | 2.7                    | 0.37                                     | 1.6                         | 0.12                  | 0.11                 | -                        | 1.7               |
| PSM40  | 57     | 550                 | 3.4                    | 0.29                                     | 2.9                         | -                     | -                    | 0.16                     | 2.9               |

*The uncertainty comes from adjusting the relevant setting within reasonable limits 10 times for the same image. The standard deviation in the mean of these 10 measurements is an estimate of the error arising from this setting.

*The uncertainty comes from analysing the same image 10 times, using the circular measure tool within reasonable limits. The standard deviation in the mean of these 10 measurements is an estimate of the error arising from manual measurement.

Fitting and Analysis of the Size Distributions

The volume-weighted size distributions measured by LD, DCS, DLS and SEM were fitted in Origin 2019b (OriginLab) by using either LogNormal or Gaussian functions.

Table S5. Mathematical expression of the descriptor parameters of the fitting functions used in Origin 2019

| Function | LogNormal | Gaussian |
|----------|-----------|----------|
| Symbols | \( w \) - log standard deviation | \( w \) - width |
|         | \( x_c \) - centre | \( x_c \) - centre |
| Mean (µ) | \( e^{\ln (x_c + \frac{1}{2w^2})} \) | \( x_c \) |
| Mode | \( e^{\ln (x_c - w^2)} \) | \( \frac{w}{2} \) |
| Standard Deviation (σ) | \( e^{\ln (x_c + \frac{1}{2w^2}) \sqrt{e^{w^2} - 1}} \) | \( \sqrt{2\ln 2w} \) |
| Full-width Half-maximum (FWHM) | \( e^{\ln (x_c) - w^2} + \sqrt{2w^2 \ln(2)} - e^{\ln (x_c) - w^2} - \sqrt{2w^2 \ln(2)} \) | \( \sqrt{2\ln 2w} \) |
LD data:

Figure S1 shows examples of fitting of size distributions as measured by LD. The fitting boundaries are shown by the pink indicators on the x axis.

Figure S1. The fitting (red line) of the modal peak for the PS125 monomodal sample, and the PSM21 and PSM40 peaks within the mixed suspension.

DCS data:

The volume-weighted size distribution was exported from the CPS software, version 11. The best fitting model was chosen based on the coefficient of determination between the data and the fit.

Peaks due to agglomeration were excluded from the analysis and only the peak relating to the non-agglomerated particle population was fitted.

In some cases, due to complex baselines in the DCS data, a fit was chosen which best described the top of the peak, which was considered accurate enough for this work, namely determination of the modal diameter and FWHM.

Figure S2. Fitting (red line) of the PS197 DCS distribution, which was agglomerated, to find the modal diameter and FWHM of the peak corresponding to the non-agglomerated particle population.
DLS data:

The volume-weighted size distribution was exported directly from the Zetasizer Software, version 7.13. The data was fitted with a LogNormal fit.

![Figure S3. Fitting (red line) of the PS125 volume-weighted size distribution as measured by DLS.](image)

SEM data:

The analysis of the SEM micrographs for the determination of the particle diameters using ImageJ is described under the Methods section of the paper. A diameter (the average of the minimum and maximum Feret diameter) was recorded for each particle, resulting in a histogram of values with a bin size of 100\(\text{th}\) of the expected diameter. The volume of a single particle in each bin was calculated using the following formula,

\[
V = \frac{4}{3}\pi d^3
\]

where \(d\) is the bin centre. This was multiplied by the bin frequency to generate a volume-weighted distribution. Figure S4 shows the distributions for PSM21, the diameter (bin centre) against the bin volume as a percentage of total volume from all the bins (volume percentage) as grey bars. The calculation of the uncertainty on the modal diameter is shown in Table S2.

![Figure S4. Fitting (red line) of the PSM21 SEM determined size distribution A) count based distribution B) volume-weighted distribution.](image)
COMPARISON OF SIZE DISTRIBUTIONS ACROSS TECHNIQUES

Figure S5: Normalised volume-weighted size distributions of LD in VLM, DCS, DLS and SEM. (a) PS60, (b) PS125, (c) PS197, (d) PS400, (e) PS590, (f) PSM2, (g) PSM21 and (h) PSM40.
IMPACT OF THE LD ALGORITHM ON THE MIXED POPULATION SAMPLE

**Figure S6.** Size distributions of the mixed sample (i.e. containing PS125, PS400, PSM2, PSM21, PSM40) as measured by LD and analysed using the VLM algorithm (continuous line) and the general purpose method (GPM, dotted line).

**VOLUME-WEIGHTED DISTRIBUTIONS FOR THE MIXED POPULATION SAMPLE**

Throughout the main text, LD distributions with a large size range, over one order of magnitude, have been displayed as density (or frequency) distributions with a logarithmic x-axis.

The volume-weighted size distribution \( v(x_n) \) with a linear x-axis is obtained from the frequency distribution \( q(x_n) \) generated by the instrument according to the formula:

\[
    v(x_n) = \frac{q(x_n)}{x_n - x_{n-1}}
\]

Where \( n \) is each of the data points in the distribution. It should be noted that datapoints acquired by the instrument were equally logarithmically spaced.

**Figure S7.** (a) LD measurement using the VLM algorithm for the mixed population sample containing PS125, PS400, PSM2, PSM21 and PSM40 displayed as a volume-weighted distribution. The insert shows the PSM2, PSM21 and PSM40 peaks, which are more difficult to see in the primary graph. (b) PS125, PS400 and PSM2 peaks of the same measurement shown using a linear scale.