Impact of particle-size polydispersity on the quality of thin-film colloidal crystals

Mariam Arif[1]*, Andrew B. Schofield[1], Fraser H. J. Laidlaw[1], Wilson C. K. Poon[1], and Job H. J. Thijssen[1]†
[1]School of Physics and Astronomy, The University of Edinburgh, Peter Guthrie Tait Road, Edinburgh, EH9 3FD, Scotland, United Kingdom

Supplementary Information

Stöber synthesis of silica nanoparticles

Batch	Ethanol (ml)	TEOS (ml)	Ammonia (35% in water, ml)	Water (distilled, ml)
1	1600	56	85	112
2	1600	56	85	112
3	1600	56	85	112
5	1600	48	85	112
7	1650	66	100	40
8	1650	76	100	40

Table 1: Synthesis recipes of silica batches

Note: Batches 1-3 were prepared using the same procedure except TEOS was added gradually (over a few seconds) during the preparation of batch 3. The amount of TEOS was increased when going from batch 7 to 8, resulting in a slight increase in average particle size (<1 nm from SEM measurement and 6 nm from DLS).

*mariam.arif@ed.ac.uk
†j.h.j.thijssen@ed.ac.uk

Batch	Recipe
4	Mixed batches 3 and 5 in a number concentration ratio of 1:1.14.
6	Mixed batches 2 and 3 in a number concentration ratio of 1:1.03.

Table 2: Recipes of mixed silica batches

Moments of measured particle-size distributions

Batch	SEM size (nm)	Skew	Excess Kurtosis
1	384	0.006	1.68
2	322	-0.582	1.92
3	381	-0.838	4.31
4	371	-0.217	-0.03
5	365	-0.128	0.25
6	360	0.024	-0.36
7	208	0.235	-0.19
8	208	0.709	1.03

Table 3: Average particle diameter, skew and excess kurtosis for particle-size distributions of the eight silica batches included in this study.

Bond-order parameter vs size and polydispersity

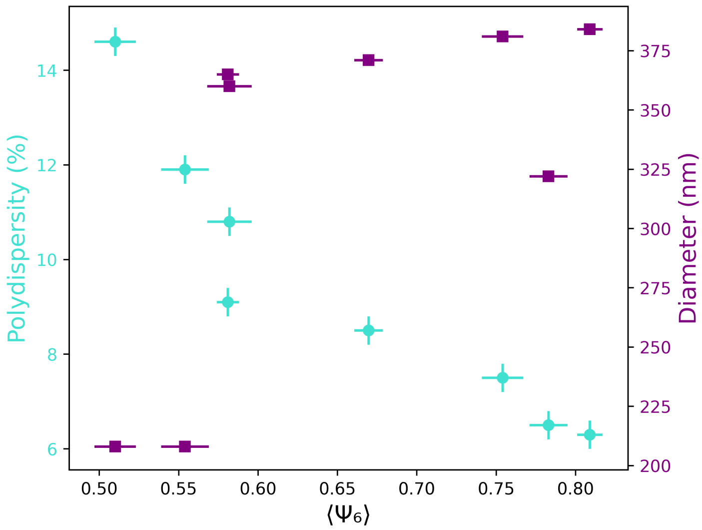

Figure 1: Average local six-fold bond-order parameter of assemblies vs. particle-size polydispersity (left axis, solid circles) and average particle diameter (right axis, solid squares).

As seen in Figure 1, the average particle size does not seem to explain variation in local order of the assemblies. For instance, the five batches with very similar average diameters (360 to 384 nm) have different local order parameters, which instead seem to be related to the difference in polydispersity of these batches.

Estimation of surface potential of silica batches

To compare self-assembling behaviours, it is important to ensure that other intrinsic particle properties, such as surface potential remains consistent across batches. To compare to relevant literature, it is important to understand how 'soft' the interparticle potential is. For practical purposes, zeta potential measurements are used as a proxy to estimate the surface potential of the batches. This approach has shown consistency with theoretical predictions and other experimental methods for determining silica surface potential [1]. Zeta potential for three silica batches ('low'=6.3%, 'intermediate'= 9.1% and 'high'= 14.6% polydispersity) is measured by Electrophoretic Light Scattering (ELS) at 25°C using the Anton Paar Litesizer-500. An optically clear silica solution is formed by adding a droplet of dispersion (10-12% silica in ethanol) to 15 ml ethanol and shaking well to ensure the particles are well dispersed. This solution is added to the measurement cell and then discarded to prepare the cell before refilling and taking measurements. The Smoluchowski approximation is used for the Henry function ($f(\kappa a)=1.5$), which has been used as a valid approximation to determine zeta potential for metal oxides in organic solvents [2, 3]. The zeta potentials for low, intermediate and high polydispersity silica batches are -47.5 mV, -51.2 mV and -48.3 mV. The colloid surfaces are negatively charged (as expected) and the dispersions are stable. The zeta potential values lie close to one another, implying that surface potential remains consistent across batches and is unlikely to influence differences in self-assembly behaviour.

Individual g(r) plots for low, intermediate and high polydispersity silica assemblies

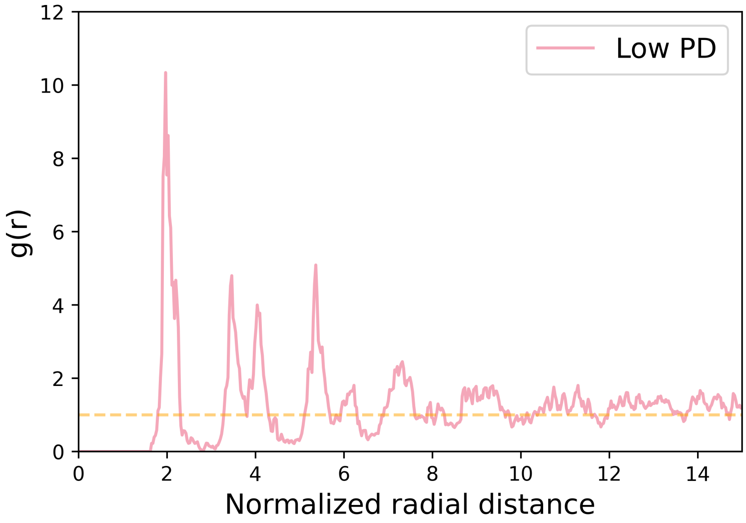

Figure 2: Normalized radial distance vs. g(r) for low (6.3%) polydispersity assembly

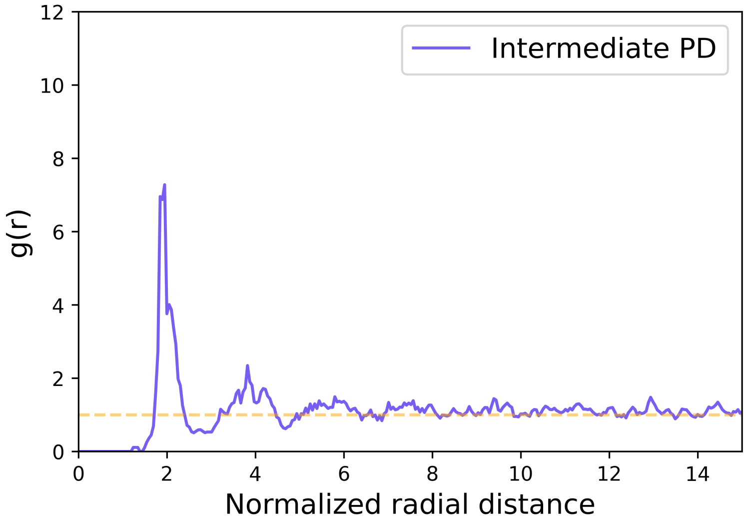

Figure 3: Normalized radial distance vs. g(r) for intermediate (9.1%) polydispersity assembly

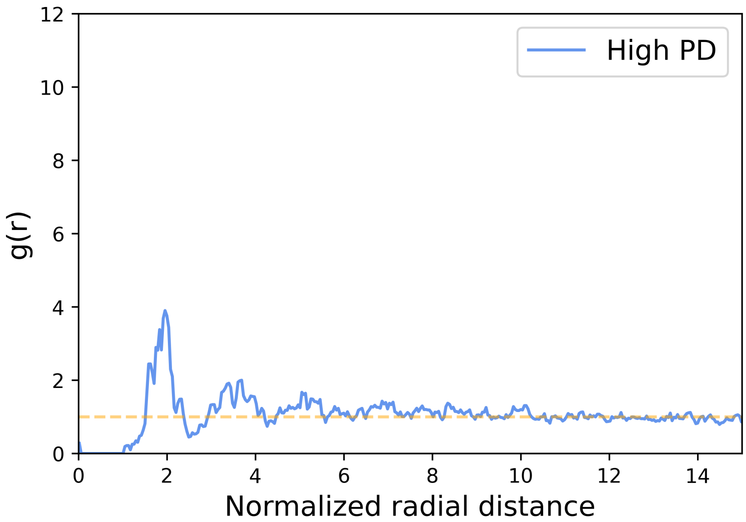

Figure 4: Normalized radial distance vs. g(r) for high (14.6%) polydispersity assembly

References

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