Advanced analysis of time-resolved and *in situ* SAXS data from evolving inorganic systems

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The formation of inorganic solid phases from solution usually follows a series of complex stages. The fact that the emergent species are often nanoparticulate in nature and metastable, necessitates their characterisation at sub-100 nm length-scales, and as *in situ* as possible. In this context, solution-based small-angle X-ray scattering (SAXS) constitutes one of the most versatile tools in studying precipitation reactions. Based on $CaSO_4$ system we demonstrate that highly complex scattering data collected in a time-resolved manner permit the extraction of detailed, cross-correlated information about structures and interactions between newly formed and evolving species in solution.

The SAXS pattern of the $CaSO_4$ nucleation and growth process showed that the very first stage involved the formation of well-defined primary particles of about <3 nm in size followed by their arrangement into domains. This was evidenced by the emergence of the structure factor contribution that gradually appeared in the scattering data. As the system developed further, these domains "collapsed", and the scattering patterns became gradually dominated by contributions from large aggregates composed of the original primary particles. In a next stage, this was followed by the growth of the primary particles within these new aggregates. This stage also corresponded with the crystallisation of these aggregates to gypsum, as evidenced by simultaneously collected the wide-angle diffraction data.

Our results indicate, that $CaSO_4$ precipitation is driven by the instant nucleation and aggregation of well-defined structural units that nucleate and grow prior to gypsum formation.