Colloidal clusters: defined supraparticles from confined self-assembly

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Small particle clusters exhibit discrete behaviour as a result of the interplay between bulk crystallization and effect of interface that separates them from their surroundings. An example is the extraordinary high occurrence of clusters of certain sizes in the mass spectrum of small noble gas and metal clusters. These clusters are termed magic clusters for their superior thermodynamic stabilities.

Recently the study of particle clusters extended to the realm of colloids. The attractive force that holds together atoms is replaced by geometric confinement of weakly interacting colloids. Small numbers of colloids pack into clusters of various symmetries [1], whereas larger clusters favour icosahedral symmetry [2]. An open question related to such colloidal clusters is whether they can also exhibit different thermodynamic stability depending on the number of their constituent building block, i.e., if the concept of magic cluster can be extended from the atomic scale to the scale of colloids.

We produce colloidal clusters of various sizes by confining colloids in emulsion droplets fabricated by microfluidics and find a large library of magic colloidal clusters with defined surface features [3]. With geometric modelling and electron tomography, we confirm that the structure of these colloidal clusters consist of closed shells of Mackay and anti-Mackay type. Free energy calculation show that these colloidal cluster exhibit superior thermodynamic stability in cases where the number of colloidal particles within the confinement affords closed shells. In contrast, if these numbers are not commensurate with a closed shell structure, the structures possess a higher free energy. Importantly, and differing from their atomic analogues, the occurrence of such magic number states is not driven by the mutual attraction of the individual building blocks. Instead, the thermodynamics in our colloidal system is entirely governed by entropy maximisation. In this presentation, I introduce synthetic requirements that are necessary for the self-assembly of magic colloidal clusters, present a detailed study on the kinetics behind the assembly mechanism using structural coloration as an investigation tool [4], and discuss pathways of the magic number colloidal clusters to accommodate defects and excess particles [5].

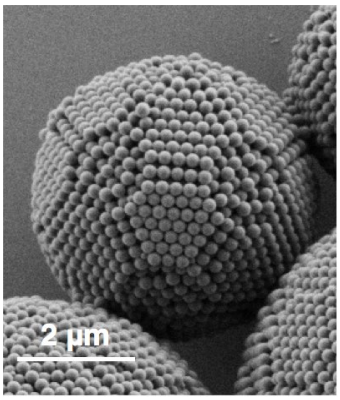

Figure 1. Exemplary magic colloidal cluster of 12 shells.

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