

Size-dependent sedimentation of nanocrystals: the role of the ligand shell structure

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The chemical, electronic, optical, magnetic, and catalytic properties, as well as the self-assembly of hybrid inorganic-organic core-shell nanoparticles depend strongly on their size and composition. Hence, there is a pressing need for a reliable method that can provide full characterisation of these particles. Although transmission electron microscopy (TEM) provides high-resolution detail of a particle's size, shape, and structure, discerning the organic materials bound on the nanocrystal surface is still a challenge due to low atomic contrast. Yet, parameters related to the overall hybrid particle (inorganic core and organic shell) properties influence particles' solubility, electronic properties, assembly, and reactivity. In this context, analytical ultracentrifugation (AUC) appears as an alternative to characterise these particles in solution, being sensitive to changes in the density and size of both core and shell components of nanoparticles. We use molecular dynamics simulations (MD) to test the validity of the Stokes-Einstein-Sutherland (SES) equation for systems of CdSe quantum dots coated with alkanethiol ligands in chloroform and explain inconsistencies between the sedimentation trends observed in AUC experiments and the ones predicted for these particles in a Stokes flow. We find that varying the size of the particle changes the structure of the ligand shell and the way it interacts with the solvent and will dictate the diffusion and sedimentation behaviours of the nanocrystals.