Local structure refinements of cuboidal and spherical $BaTiO_3$ nanocrystals utilizing accurate shape effects

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As materials become increasingly complex and the miniaturization of functional materials continues, the ability to characterize intricate structural details is key to developing robust structure-property relationships. In the structural refinement of nanoparticles, discrete atomistic modeling can be used for small nanocrystals (< 15 nm), but becomes computationally unfeasible at larger sizes, where instead small-box modeling is usually employed. However, the effect of the nanocrystal's shape is often ignored or accounted for with a spherical model regardless of the actual shape due to the complexities of solving and implementing accurate shape functions. Recent advancements have provided a way to determine the shape function directly from a pair distribution function calculated from a discrete atomistic model of any given shape, though this approach is still limited to small size regimes. In order to implement accurate shape functions in small-box refinements where the structures of larger nanocrystals (20-100 nm) can be refined, we developed a method to generate scalable analytical descriptions of shape functions for a given geometry. We deployed this approach in the structural analysis of X-ray and neutron pair distribution functions of $BaTiO_3$ nanocubes and nanospheres in the 10-100 nm size regime. It was found that the use of accurate shape functions yields higher quality refinements, and for the cuboidal nanocrystals in particular, more accurate nanoparticle sizes. The method, results, and the influence of the shape effect on structural parameters, as explored through simulated and experimental data, will be discussed.