The Shape of Small Gold Nanoparticles: Force Fields vs. DFT

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Abstract: Comprehending the growth and shape transformation of colloidal metal nanocrystals' thermodynamic and kinetic equilibrium (e.g., knowledge of shape and its transformation pathways can help selectively synthesize desired metal nanocrystal sizes and shapes) would benefit many potential applications. We leveraged replica-exchange molecular dynamics (REMD) simulations to probe the minimum free-energy shapes of Au nanoclusters at magic sizes of 55 and 147. Common neighbor analysis (CNA) has been implemented to determine the shape and the simulation results revealed a new unique shape, hollow Ih, which has hollow Ih core and unreported distinct CNA signatures. In addition, we explored the effect of temperature on the shape distribution of nanocrystals and found the choice of force fields significantly influences the final distribution, but hollow Ih appears in all 4 types of force fields we used. With density-functional theory calculation, we proved that the hollow Ih is more favored than Ih in Au147, and the embedded atom method (EAM) force field has limitation to accurately describe the atomic interaction in small metal nanocrystals, especially in energy orders and melting points.