

The Nanoscale Forces behind Crystallization by Oriented Aggregation

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Crystal growth by assembly of small particles or clusters as opposed to ion-by-ion is a recently recognized type of growth impacting our understanding of natural mineralization processes, and holding promise for novel materials design. Oriented aggregation (OA) is an important case where larger crystals grow by the oriented self-assembly of smaller ones. Materials and conditions that trigger this pathway and the enabling interparticle forces are poorly understood. Growth by OA is characterized by nanocrystals that are generally stable with respect to ion-by-ion dissolution or growth, interacting under net attraction and forces that tend to co-align nanocrystal lattices at short range. Successful attachment is predicated upon near-perfect co-alignment. A metastable solvent-separated "captured" state typically persists as particles sample mutual orientations until co-alignment is achieved, where the energy barrier to solvent expulsion and interparticle bonding is apparently lowest.

Our team is measuring and simulating the interaction forces between single crystal faces of model minerals in aqueous solution. Dynamic force spectroscopy (DFS) using nanoengineered single-crystal single-face force probes for ZnO(001)-ZnO(001) and muscovite(001)-muscovite(001) reveals a rupture force that varies on the order of pN/nm² with azimuthal co-alignment. Classical density functional theory simulations were developed to assess the balance of microscopic hydration, dispersion, electrostatic, entropic, and ion correlation forces underlying OA observed for anatase TiO₂ nanoparticles in acidic aqueous solution. Analysis of the distance dependence of various facet-specific interactions shows that ion correlation forces are responsible for face selectivity and co-alignment while solvent-separated; the attachment barrier is largely due to steric hydration forces from structured intervening solvent. We continue to explore the molecular underpinnings of OA through systematic examination of ionic strength, electrolyte type, crystallographic face, and azimuthal orientation effects, and seek convergence between development and validation of atomic-to-mesoscale models against nanocrystal interaction forces measured directly in aqueous solution.