558e Alignment of Nano-Crystallites by Anisotropic Van Der Waals Forces

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While it is widely accepted that van der Waals forces drive the aggregation of small particles, the reasons that superlattice arrangements form are unclear. For example, nanometer size aggregates of barium titanate and cadmium selenide crystallites are often organized with their crystallographic planes in registry with one another. In some instances, superlattices form despite the presence of soft coatings that preclude 'registration' by crystal facets. Here we show that orientation can arise from anisotropic van der Waals forces as small particles rotate relative to one another in the late stages of the aggregation process. Thus, while the balance between van der Waals attraction, viscous flow, and Brownian motion determines the rate of approach, van der Waals torque induces alignment. First we derive an expression for the anisotropic van der Waals interaction between two crystallites based on Hamaker's microscopic theory. When this is combined with a probabilistic interpretation of the balance between rotary Brownian motion and torque, it shows that crystallites will align with their crystallographic axes parallel with one other - where the van der Waals energy is a minimum. Good agreement between theory and experiment is found for BaTiO₃ and CdSe nano-crystallites.