

## Observing Nucleation Fluctuations with In Situ AFM

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Classical nucleation theory (CNT) predicts that nucleation of crystals from solution requires a population of sub-critical molecular clusters that form through dynamic statistical fluctuations. These clusters are expected to occur in any solution, and their observation would provide direct confirmation of the classical nucleation theory. However, these clusters have been extraordinarily difficult to observe, due to their inherent scarcity and their transitory nature.

Here, we introduce high-speed *in-situ* atomic force microscopy (AFM) as a method for directly imaging subcritical clusters of aluminum hydroxide at a mica-water interface. With this technique, we are able to determine the size-distribution of subcritical clusters and track the fluctuations of individual clusters over time.

When imaging a cleaved mica surface in the presence of  $\text{AlCl}_3$  aqueous solutions, we observe single-molecule adsorbates. Based on concentration-dependence, streaming-potential measurements, and *ab-initio* molecular dynamics, we conclude that the adsorbates are surface-bound hydrated aluminum ions, and that the surface promotes hydrolysis of these ions. When the solution saturation is increased, we find a population of dynamic molecular clusters emerges, with sizes of up to  $4.0 \text{ nm}^2$ . The concentration of clusters drops off exponentially with size, in general agreement with the size-dependant free energy of cluster formation predicted by CNT. The clusters also fluctuate in size in a manner that is consistent with CNT. Further increases in supersaturation leads to growth of a monolayer of crystalline aluminum hydroxide through cluster-coalescence.

We arrive at a description of the nucleation pathway in which the surface enhances nucleation rates by concentrating a dense-liquid layer of aluminum at the mica-water interface, and that classical cluster fluctuations occur within this layer. However, the high concentrations of clusters favors a late-stage crystal growth pathway that is dominated by cluster coalescence, rather than ion-by-ion addition.