On the behavior of hydrated $CaCO_3$ clusters in supersaturated solutions

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Interest in the molecular scale processes underlying the onset of mineral formation is on the rise due to the detection of nanoscale ion aggregates in concentrated aqueous solutions. As the archetypal system for "pre-nucleation" clusters, the early stages of calcium carbonate have been intensely scrutinized from both theoretical and experimental perspectives. The definition of a pre-nucleation cluster, initially described as being relatively constrained in size and thermodynamically stable with respect to both dissolution and growth [1], is currently evolving and is now identified with a rather broad distribution of aqueous species whose continued growth is restricted by diffusion limitation [2]. This reinterpretation is due in part to the results of molecular dynamics simulations that suggest an exponentially decaying cluster size distribution rather than monodisperse cluster species [3]. The simulated size distribution is also consistent with the results of cryo-TEM [4] and the predictions of classical nucleation theory (CNT).

This work [5] uses atomistic and coarse-grained simulation techniques to explore the formation of clusters from supersaturated solutions. The results of molecular dynamics simulations indicate the accessibility of a metastable liquid-liquid binodal/spinodal. Coalescence and partial dehydration of the dense liquid droplets results in the formation of a solid phase whose structure is consistent with amorphous calcium carbonate. Coarse-grained simulations of fluid-fluid separation in the spinodal regime produce cluster size distributions that are qualitatively similar to those produced from molecular dynamics simulations of spontaneous phase separation in the $CaCO_3$ system [3]. The presence of a dense liquid phase of CaCO3 is also supported by recent experimental efforts [6], which suggest an entropy driven phase transition may precede solid $CaCO_3$ formation under certain conditions.

[1] Gebauer *et al* (2008) *Science* **322** 1819-1822. [2] (2012) *Faraday Discuss*. **155**, 139-180. [3] Demichelis *et al* (2011) *Nat. Commun*. **2**, 590. [4] Pouget *et al* (2009) *Science* **323** 1455-1458. [5] Wallace *et al* (2013) *Science* **341** 885-889. [6] Bewernitz *et al* (2012) *Faraday Discuss*. **159** 291-312.