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Recent advances show that nucleation of crystalline phases from dilute solutions often involves the formation of intermediate disordered states: clusters, droplets, amorphous nanoparticles, polymorphs etc [1]. It remains unclear how the intermediate states affect the predictions of the classical single-step nucleation theory, in terms of activation barrier, rate of nucleation, or critical cluster sizes. Progress is hampered by the difficulty to reach sufficient resolutions (<1nm, <<1s), without perturbing the metastable process.

Here, we overcome this issue using in situ x-ray scattering, and report nucleation rates upon formation of different nanocrystals in solution (luminescent YVO_4:Eu, magnetite Fe_3O_4), where an intermediate nanostructured amorphous network is evidenced [2,3]. We find how the amorphous precursor impedes nucleation at the nanometer scale, and limits the size of the nanocrystals. The clarification of the role of the intermediate nanostructure clarifies why the predicted nanocrystal sizes are overestimated by several orders of magnitudes by classical theories.

Reference:

[1] J. J. D. Yoreo *et al.*, Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science*. **349**, aaa6760 (2015).

[2] B. Fleury *et al.*, Amorphous to Crystal Conversion as a Mechanism Governing the Structure of Luminescent YVO4:Eu Nanoparticles. *ACS Nano*. **8**, 2602–2608 (2014).

[3] J. Baumgartner *et al.*, *submitted*