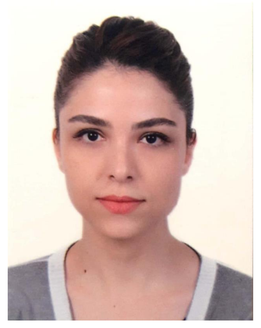
wetsus
european centre of **excellence**
for sustainable **water technology**

Characterisation and tuning of DOLLOPs in potable waters



Talie Zarei

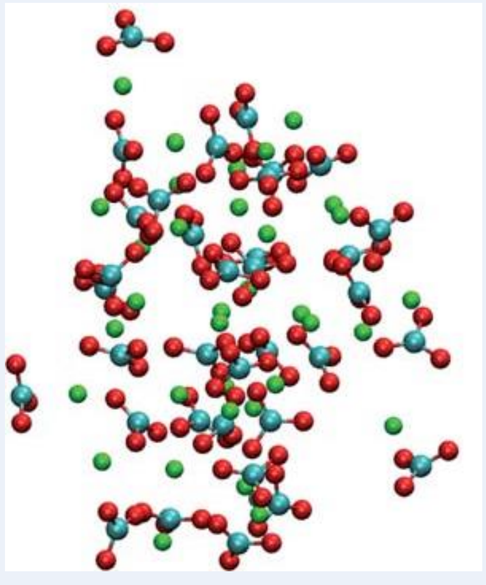
talie.zarei@wetsus.nl

Motivation

Thermodynamically-stable, nm-sized prenucleation clusters in undersaturated $CaCO_3$ solutions consisting mostly, but not entirely, of $CaCO_3$ can be accounted for as much as half the calcium present in solution [1]. These “sloppy” objects have earned the felicitous name “DOLLOPs” (Dynamically-Ordered Liquid-Like Oxyanion Polymers) [2] (Fig. 1a). These hydrated clusters are found to aggregate into much larger (4–100 nm) particles [3] (Fig 1b and Fig. 2), forming a liquid emulsion at neutral pH [4]. Little is known about the concentration, size distribution, structure and dynamics of DOLLOPs in potable waters. Investigating these parameters and the ratio of Ca^{2+} in DOLLOPs compared to the overall Ca^{2+} concentration offers the chance of extending the parameters of water quality. The chemistry of aqueous systems [5] can be understood and dealt with more accurately if DOLLOPs are taken into account and characterized properly. Moreover, it has been suggested recently that DOLLOPs provide the basis for a plausible mechanism for magnetic treatment based on the gradient of the applied field rather than its absolute strength [6, 7].

Technological challenge

DOLLOPs are small, fragile objects in relatively low concentrations (estimated to be in the order of 10^4-10^5 particles per mL), which makes the characterization of the number, size distribution and structure of DOLLOPs a big challenge. They have to be measured in solution, since filtering and drying them will irreversibly change their properties. In order to achieve this goal, state-of-the-art liquid separation (FFF) and detection techniques (MALS-ICP) will have to be applied.



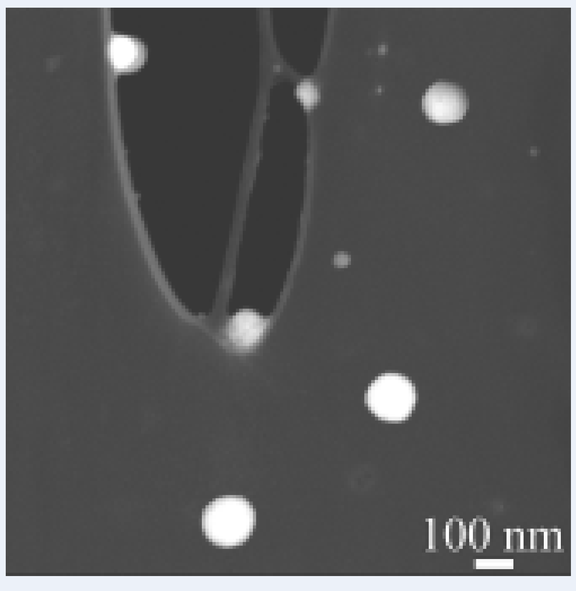


Fig 1. a) Snapshot of amorphous calcium carbonate nanoparticles taken from molecular dynamics simulation (left) [2] and b) TEM (right) (white spheres) [3].

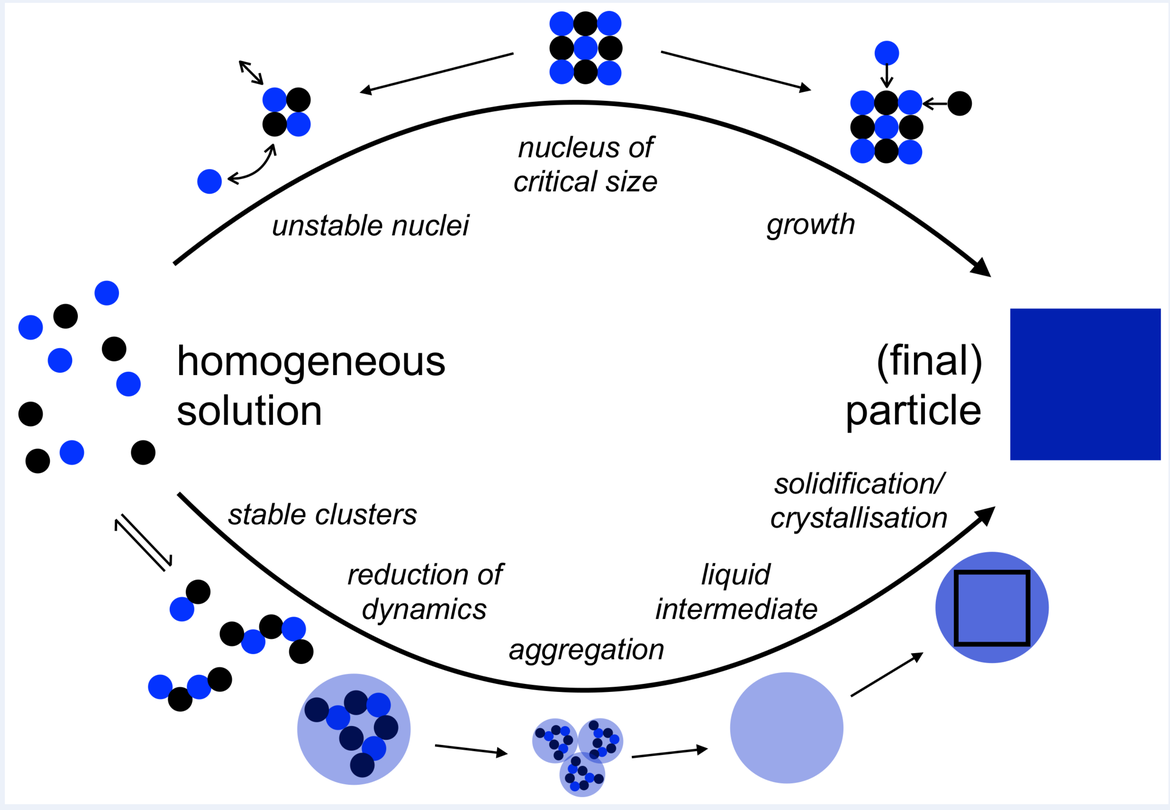


Fig. 2 Schematic illustration of the mechanism of nucleation of DOLLOPs according to classical nucleation theory (CNT, top) and the pre-nucleation cluster (PNC) pathway (bottom) [8]. The PNC pathway has gained more attentions during the last years and it can be more rationalized for creating DOLLOPs in $CaCO_3$ solutions in different experiments.

Research goals

The goal of this project is to establish a new, more precise definition of the hardness of water. This will be achieved by characterizing how Calcium, Magnesium and Carbonate are dissolved in water, namely how much is dissolved in ionic form, and how much in colloidal (“DOLLOPs”) form. In order to better understand the dynamics, shape, structure and stability of DOLLOPs and their agglomerates (see Fig. 2), next to investigating natural waters, DOLLOPs will also be created in the lab. Moreover, shifting their population between ionic and colloidal phase using physical (e.g. magnetic fields) and chemical methods (e.g. pH change) will be investigated.

[1] D. Gebauer, A. Völkel and H. Cölfen, *Science* **322** (2008) p.1819.
[2] R. Demichelis, P. Raiteri, J.D. Quigley and D. Gebauer, *Nat. Comm.* **2** (2011) p.590.
[3] Eshel Ben Jacob, Tel Aviv University, *private communication* (2010)
[4] S.E. Wolf, L. Müller, R. Barrea, C.J. Kampf, J. Leiterer, U. Panne, T. Hoffmann, F. Emmerlingand and W. Tremel, *Nanoscale* **3** (2011) p.1158.
[5] A. Ahmad, S. van de Wetering, *H_2O-Water Matters* (2018), 24-27.
[6] Coey, J.M.D., *Phil. Mag.* **92** (2012) 3857–3865.
[7] M. Sammer, C. Kamp, A.H. Paulitsch-Fuchs, A.D. Wexler, C.J.N. Buisman, E.C. Fuchs, *Water* **8** (2016) 79.
[8] D. Gebauer, *Minerals* **8**.5 (2018) 179.