

Molecular dynamics simulations of amorphous calcium carbonate nanoparticles

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Importance

In Earth Sciences and Geoengineering, knowledge on crystal nucleation mechanisms is crucial to:

- quantify fluxes in biogeochemical cycles
- unravel the timing and rate of different geological processes
- unravel the physical and chemical conditions during crystal formation
- to evaluate crystal origin and quality for proxy for paleo-environmental conditions
- to optimize crystal formation for subsurface remediation, stabilization and CO₂ sequestration.

Research question and approach

What is the size, shape and structure the first calcium carbonate (CaCO₃) nanoparticles that form in solution? Answering this question is a challenging prospect experimentally¹.

Atomistic simulation techniques, in particular molecular dynamics can be used to estimate structural and thermodynamic properties of ACC², and the importance of water in ACC nucleation³. In this work, we use classical molecular dynamics to study the behaviour of ACC clusters and free ions (Ca²⁺, CO₃²⁻) in water.

Conclusions

- CaCO₃ nanoparticles form and aggregate most rapidly at ideal Ca:CO₃ = 1:1 ratio
- At non-ideal ratios, they remain < 10 nm for up to hours (Fig. 1)
- There is a trend in the simulated particles to reach charge neutrality (Table 1)
- Simulations show
 - the size of nanoparticles experience a lot of variation (Fig 3)
 - all the nanoparticles are more stable than the ions in solution (Fig 4).
- **This means that non-stoichiometric (charged) nanoparticles are stable.**

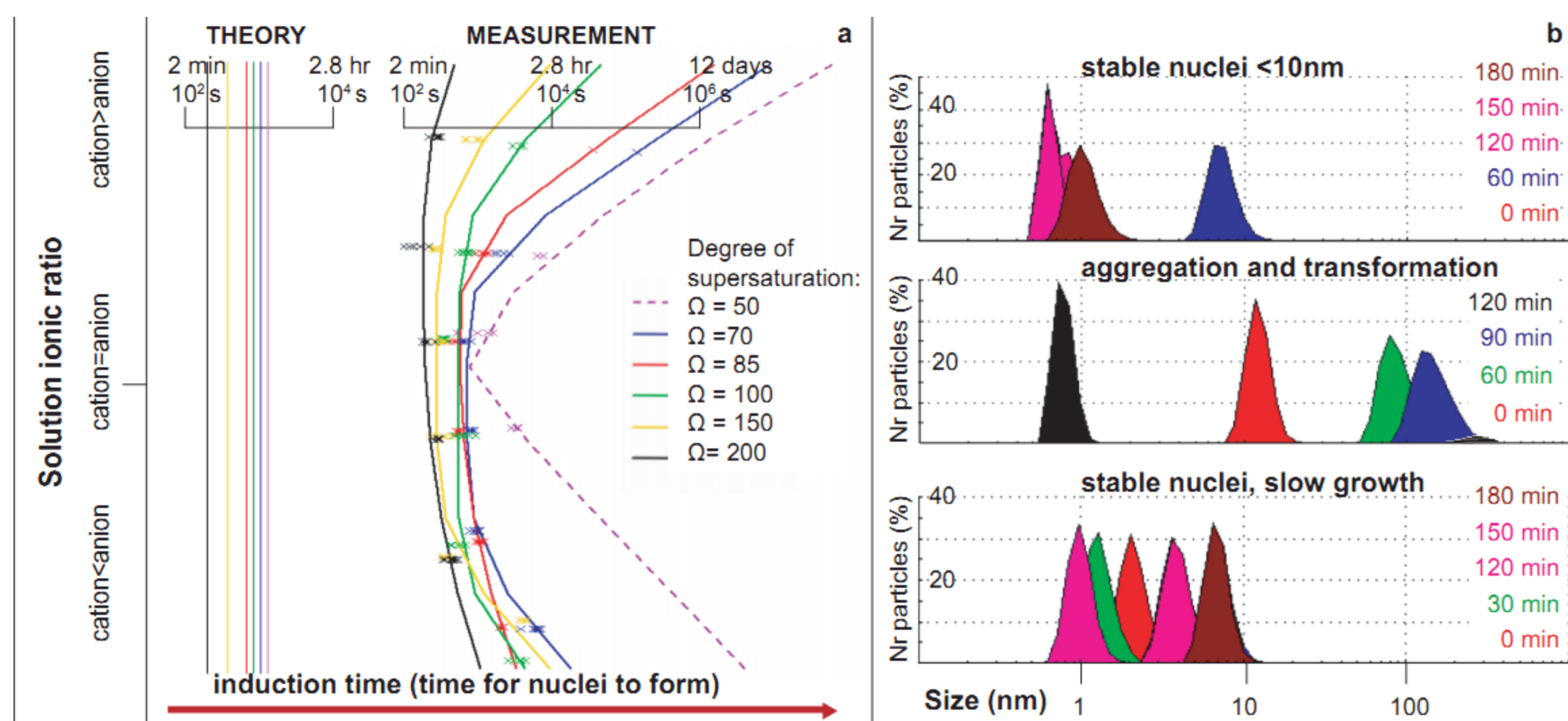


Figure 1 Ionic ratio affects the timing of nucleation (a) and how the newly formed particles grow (b). Measurements in (a) obtained with Polarized-light Optical Microscopy (POM) and time includes growth up to 40 μm, and in (b) using Dynamic Light Scattering, detection limit ±0.3 nm. Ω indicates degree of supersaturation w.r.t. calcite.

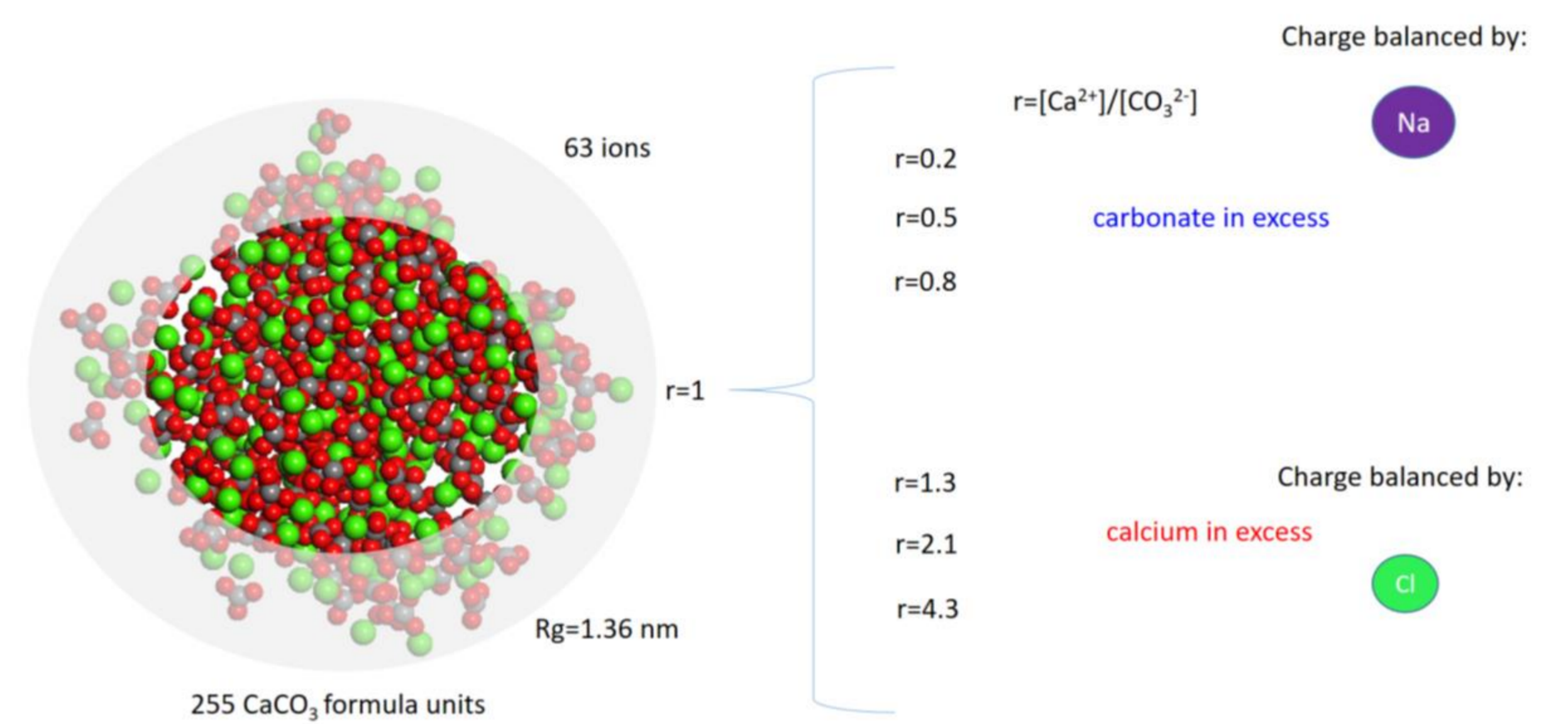


Figure 2 Simulation idea

We started from a randomly generated ACC neutral cluster of a size close to the seeing in experiments. From that structure, we have extracted some of the most external ions to reproduce the solution's ionic ratio in the most external regions of the particle. The resulting clusters have either more Ca²⁺ or CO₃²⁻.

Molecular Dynamics simulation details

- Simulation package: DL_POLY 4.09.
- Classical MD, NPT ensemble; x, y, z periodic box. Force Field from Demichelis *et al.*²
- Nosé–Hoover thermostat and barostat (timestep 1 fs, relaxation times of 0.1 ps and 1 ps)

$$R_g^2 = \frac{1}{M} \sum_{i=1}^N m_i (r_i - r_{COM})^2$$

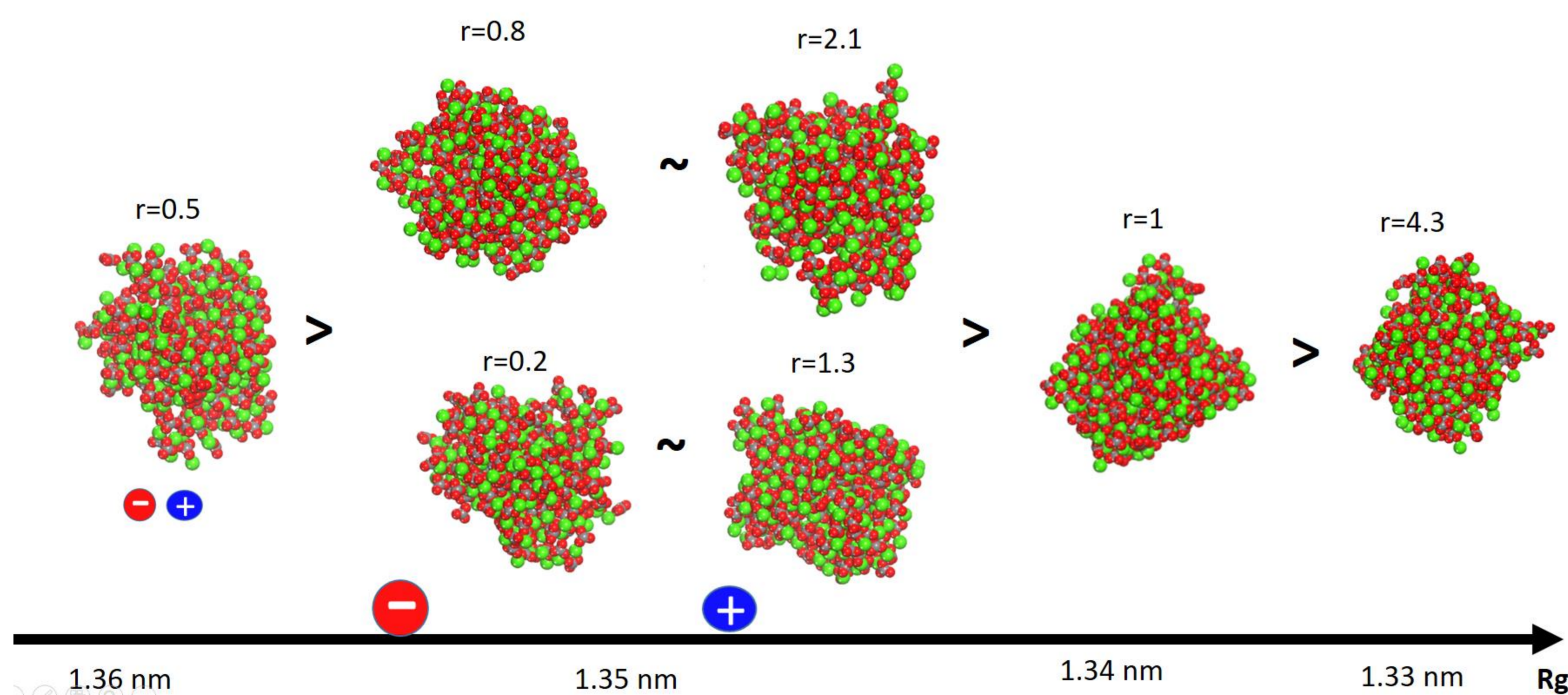
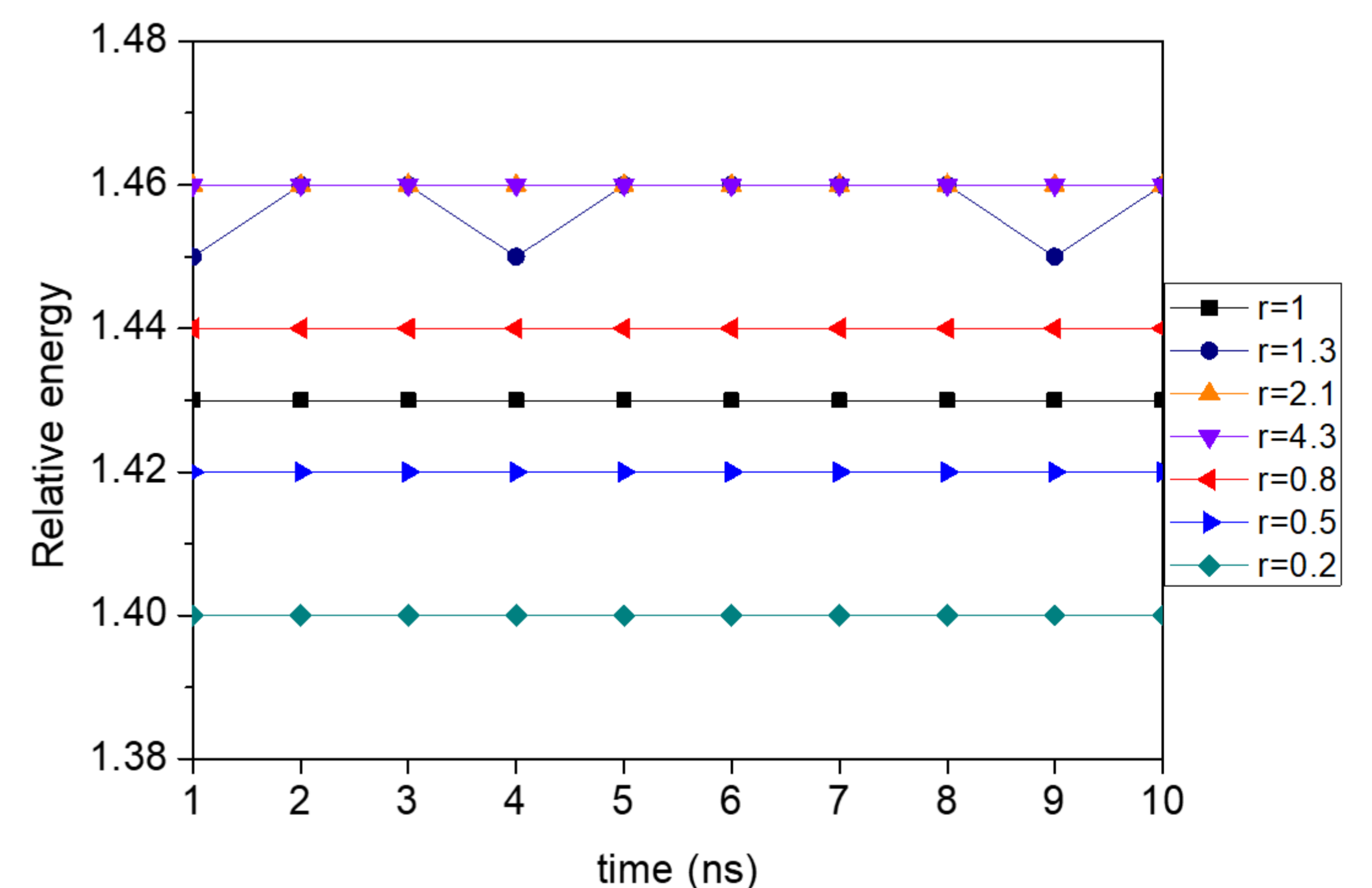


Figure 3 Final size distribution after 10 ns of simulations

Table 1. ACC clusters composition.

r _{aq/ion}	t=0 ns		t=10 ns	
	Ca ²⁺	CO ₃ ²⁻	Ca ²⁺	CO ₃ ²⁻
0.2	205	255	201	206
0.5	224	255	226	226
0.8	238	255	241	249
1	255	255	253	251
1.3	255	238	245	233
2.1	255	224	234	219
4.3	255	205	207	200



$$\text{Relative energy} = \frac{\text{Energy of the simulated system}}{\text{Energy of a system with all ions in solution}}$$

Figure 4 Relative stability of the particles after 10 ns of simulations

References

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