# Stable prenucleation clusters in lattice models of crystal growth

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Our understanding of how crystals grow from solution is often framed in terms of classical nucleation theory (CNT). This simple theory describes the balance between surface and bulk free energies to form a nucleation barrier, dictating that only solute clusters larger than a critical size are stable against dissolution. This leads to the concept of nucleation as a rare event, i.e. spontaneous formation of a post-critical nucleus.

It is therefore surprising that experiments on calcium carbonate ($\mathrm{CaCO_3}$) growth solutions have revealed the presence of stable *prenucleation* clusters [3]. In a recent paper [1] we performed and analysed detailed atomistic simulations leading us to postulate that growth of $\mathrm{CaCO_3}$ is barrierless. Within this picture, the formation of stable prenucleation clusters emerges as unrestrained growth of chain-like solute clusters (essentially diffusion limited aggregation), tempered by competition for $\mathrm{CO_3^{2-}}$ binding sites. The competing species are $\mathrm{HCO_3^-}$ ions, arising as a natural consequence of solution pH. These act as mobile chain terminators, inhibiting further growth. This picture may explain some features of biomineralisation, the mechanism by which nature influences $\mathrm{CaCO_3}$ growth. Complementarity between these solute chains and biopolymers provides a route for nucleating biocomposite materials with highly desirable mechanical properties.

Atomistic simulations have been able to simulate the formation of these ions at high concentrations, but are limited in terms of timescale. Our understanding of the subsequent nucleation event is very limited. We are therefore interested in developing simple models from which this particular non-classical nucleation and growth mechanism can emerge. Results will feed downstream into design of new large-scale atomistic simulations, and ultimately new experiments in controlling growth.

A basis from which to start is the lattice-gas Potts (LPG) model of Duff and Peters [2]. This consists of a cubic lattice on which each site $i$ is occupied by either a ’solute’ particle ($m_i = 1$) or a ’solvent’ particle ($m_i = 0$). Each solute molecule can additionally posses one of $Q = 24$ orientational states $s(i)$. The system has a Hamiltonian of

$$H = - \sum_{\langle i,j\rangle} m_i m_j \left\{ [K - A/Q] + \delta_{s(i),s(j)} A \right\} - \sum_{\langle i,j\rangle} (1-m_i)(1-m_j) K',$$

where $K$ controls the quality of the solvent, $K'$ the melting temperature of the ideal crystal and $A$ the strength of an orientation-dependent nearest-neighbour interaction between solute particles. When all sites are occupied by aligned solute molecules, the system is analogous to an ordered crystal. Monte-Carlo simulations in the semi-grand ensemble (SGE) demonstrate that this crystal can grow from the solvent via CNT, or via a non-classical mechanism in which a disordered aggregation of solute grows to a significant size before undergoing ‘crystallisation’.

The goal of this project is to extend the LPG model such that stable prenucleation clusters emerge. The practicalities of the project will involve modification of an existing computer code, or (depending on the student) development of a new program for performing simulations on this system. On a mini-project timescale, the project deliverables will be;

- Parameterising the existing two-species model to exhibit barrier-less growth.
- Introducing a third species to act as the mobile growth terminator.
- Conducting extended SGE MC simulations to characterise nucleation in the resulting model.

Should a student be interested in continuing this into a PhD project, future work would examine the energetics and kinetics of crystal growth mechanisms which emerge from this and related models. Application of path sampling techniques to gain quantitative data on nucleation rates would be the ultimate goal. Collaboration with molecular simulators would be beneficial, with the possibility to inform and equivalent studies on models with molecular detail. There is also scope for more detailed theoretical work using mean field approaches.

This project would suit a student with good programming skills and an interest in computational statistical mechanics.

## REFERENCES

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