Partial disorder 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 theory operates under the assumption that a growing solid adopts the same internal structure the final bulk crystal. This CNT model can be a good fit to experimental data, but subsequent calculations of crystal nucleation rates are often incorrect by many orders of magnitude. Combined with growing simulation evidence, this suggests that even very simple crystals can nucleate and grow via non-classical mechanisms which are yet to be fully understood.

A particular research effort at Warwick is the study of mechanisms associated with the growth of shells, teeth and bone. These are highly complex, involving bio-molecular templates, and other protein-mediated processes which preferentially select particular non-classical growth pathways. The resulting bio-composite materials have desirable properties, and exhibit structural complexity beyond anything which can be manufactured in a laboratory. Improved understanding of these processes could ultimately improve manufacturing of advanced materials.

Modelling of these processes at the atomic and molecular scale can be prohibitively expensive. Fortunately, a number of simple lattice models have recently been proposed from which non-classical growth pathways emerge [1, 2]. One example is the lattice-gas Potts (LPG) model of Duff and Peters [1]. 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

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

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 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 to three species to enable formation of a *partially* disordered metastable crystal. This is a solid in which ordered and disordered sub-lattices of different species interlock, representing minerals such as vaterite. A number of simple Hamiltonians can be envisaged to achieve this. Growth pathways which visit these states as an intermediate would mimic the growth of calcium carbonate, a common biomineral.

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;

- Validation of this code against existing results for the two-species model.
- Location of parameters for which a partially disordered crystal is stable in a three-species model.
- Mapping the phase diagram of the three-species model using direct coexistence techniques in the semi-grand ensemble.

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

[1] N. Duff and B. Peters. Nucleation in a Potts lattice gas model of crystallization from solution. *J. Chem. Phys.*, 131(18):184101, 2009.

[2] S. Whitelam. Nonclassical assembly pathways of anisotropic particles. *J. Chem. Phys.*, 132(19):194901, 2010.