P.38 Lattice model of nucleation via partially disordered precursor

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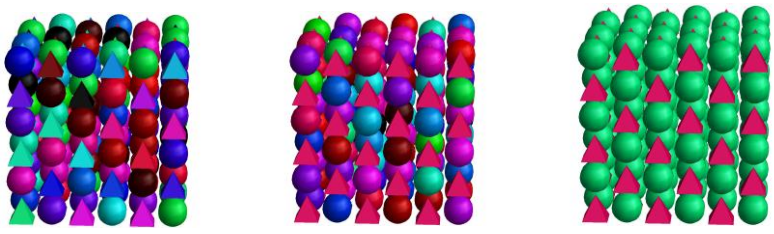
Nucleation is considered one of the fundamental mechanisms of phase transitions and has been studied for over a century in a broad range of systems. The study is largely motivated by the importance of control of not only the rates of phase transitions but also the size, morphology and other properties of the products of nucleation. Despite the large volume of experimental, theoretical and numerical findings, a number of key questions in nucleation theory, e.g. those regarding rates [1], pathways [2] and control strategies [3], remain open.

The process of biomineralisation, whereby nucleation and growth are mediated by organic components, appears to progress with a high degree of precision [4], which serves a natural example of self-assembly – a phenomenon of great technological interest [5]. The prototypical system for study of biomineralisation and polymorph selection is calcium carbonate ($CaCO_3$), where some degree of controlled assembly has been demonstrated in a laboratory [6–8]. Recently [9], it has been shown that crystallisation of calcite – the most stable polymorph of CaCO3 at ambient conditions – may proceed via an amorphous precursor followed by vaterite – a metastable polymorph whose molecular structure is characterised by a degree of structural disorder [10].

Some important insights into nucleation of $CaCO_3$ have been gained through molecular dynamics (MD) simulations [11–13], however, detailed atomistic models tend to be prohibitively expensive to probe the process directly. More rigorous studies [14–16], have used lattice models to show existence of amorphous precursors in assembly of anisotropic particles. To our knowledge, however, the amorphous and partially disordered precursor pathway has not been previously captured.

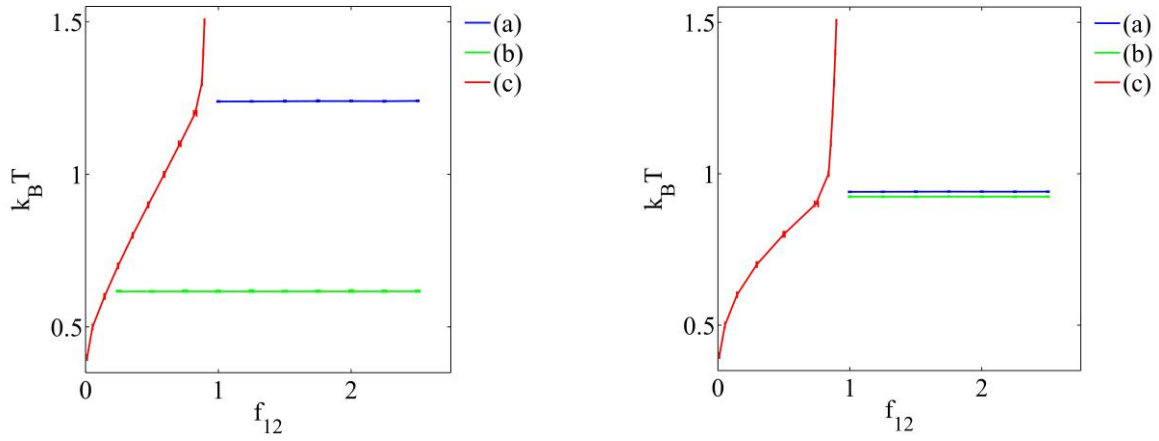
In the following contribution we present a lattice model of nucleation from solution, where the solute may take disordered, ordered or semi-ordered forms. We further show that, in the limit of slow growth, the transition from solvent rich to ordered crystalline state proceeds via the two polymorphs.

We study a three component system in semigrand ensemble on a cubic lattice with diagonal neighbour anisotropic interactions. We choose interactions which allow us to control the stability of the partially disordered polymorph and obtain corresponding phase diagrams using a variant of the Wang-Landau method [17] and histogram reweighting. By applying equilibrium path sampling [18], we show that the degree of disorder in solute nuclei, grown under moderate subcoolings and supersaturations, varies with their size.



(a) Disorder (D) (b) Partial disorder (PD) (c) Order (O)

FIG 1: Solute polymorphs



(a) Unequal anisotropic interactions (b) Equal anisotropic interactions

FIG. 2: Phase diagrams for different anisotropic interaction strengths, where f_{12} is the solute saturation parameter. Coexistence lines shown: (a) D and PD; (b) PD and O; (c) solute and solvent.

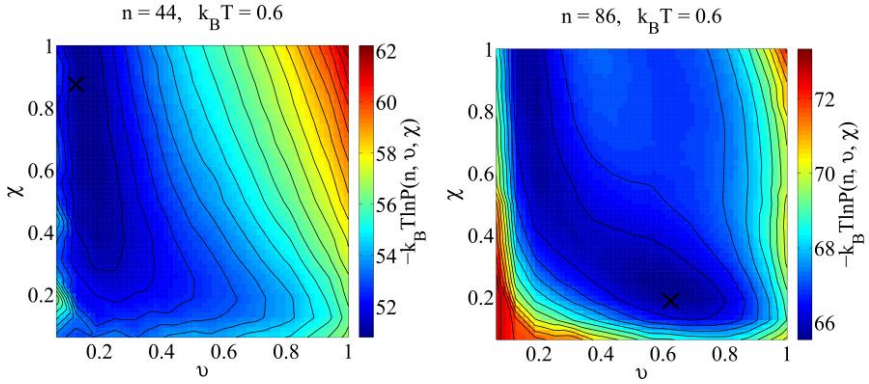


FIG. 3: Projections of free energy surfaces onto (v, x) plane, showing the transition of the local minimum from total disorder to partial disorder. Here n is the number of particles in the largest cluster present in the system, while v and x are parameters characterising the degree of orientational order within the cluster. The two orientational order parameters are such that state v = 1; x = 1 corresponds to perfect order, state $v \approx 0$; x = 1 - to disorder and state v = 1; $x \approx 0$ – to partial disorder. Contours are drawn at intervals of 1:0k_BT and black cross shows the coordinate of the local minimum.

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