



- We have only rules of thumb with which to predict how a material will crystallize, chief among which is Ostwald's rule of stages. It states that the first phase to appear upon transformation of a parent phase is the one closest to it in free energy. Although sometimes upheld, the rule is without theoretical foundation and is not universally obeyed, highlighting the need for microscopic understanding of crystallization controls.
- Here we study in detail the crystallization pathways of a prototypical model of patchy particles. The range of crystallization pathways it exhibits is richer than can be predicted by Ostwald's rule, but a combination of simulation and analytic theory reveals clearly how these pathways are selected by microscopic parameters. Our results suggest strategies for controlling self-assembly pathways in simulation and experiment.
- Left: Free energy as a function of cluster size ( $N$ ) and crystallinity ( $N_c$ ). Under these conditions the thermodynamically favored pathway (black line) is the direct transformation from vapor (V) to solid (S). However, it is possible to selectively access different nucleation pathways by tuning the relative rates of rotation and translation. For fast rotations (red) the direct ("classical") pathway is observed. An indirect ("non-classical") pathway is seen in the case of slow rotations (blue).

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