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Soft matter self-assembly driven by specific and nonspecific attractions: dynamic pathways and the Ostwald rule of stages¹

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Ostwald's rule of stages is one of the few rules-of-thumb we possess that suggests the dynamical pathway a material will take when crystallizing. It states that bulk phases intermediate in free energy between the parent phase and the stable solid will emerge before establishment of the stable solid. Although widely applicable, this rule is frequently seen to break down in experiments and computer simulations, showing it to be without theoretical foundation. A first step in going beyond this rule is to understand why it breaks down. Here we test Ostwald's rule of stages in a statistical mechanical model of crystallization. Our model describes particles that are prototypical of a class of materials (such as proteins and patchy nanoparticles) able to form solid phases stabilized by directional attractions, as well as sparse and dense fluidlike phases. We find that the rule holds in certain regimes of parameter space and breaks down in others. Importantly, its breakdown can be anticipated using simple arguments. We show that the qualitative crystallization pathway of the model depends in general on both the thermodynamic landscape prescribed by inter-particle interactions and on the relative rate of particle rotations and translations. This observation emphasizes that any general rule of crystallization must account for both thermodynamic and dynamic factors.

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