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**Non-classical nucleation theory in colloidal fluids: Kinetically persistent precursors** M.A. DURAN-OLIVENCIA, P. YATSYSHIN, Department of Chemical Engineering, Imperial College London, London, UK, J.F. LUTSKO, Center for Nonlinear Phenomena and Complex Systems, Universite Libre de Bruxelles, Brussels, Belgium, S. KALLIADASIS, Department of Chemical Engineering, Imperial College London, London, UK — In recent years, a flurry of experimental observations has suggested that most phase transitions occur in a multistage manner, via intermediate phases. These precursors to the final phase are generally understood as the local minima of the free energy of the system. Inherently, the classical paradigm of nucleation has no capacity to describe neither the origin nor the role played by these precursors in the nucleation pathway. In this work, we present a systematic theoretical framework capable of describing the precursor phases in a self-consistent way. We demonstrate that nucleation precursors can appear even in situations involving a single free-energy barrier. This contradicts previous phenomenological approaches, which always characterise intermediate phases as the minima of a complex free-energy landscape. We show that a kinetically-induced mechanism temporarily stabilizes an intermediate phase, which thus is not the result of a local minimum of the free energy but results from the entropic cost of cluster formation. Moreover, the appearance of precursors does not seem to influence the overall nucleation time, which is governed by the free-energy barrier. The mechanism uncovered in this study can be used to explain recently reported experimental findings in crystallization.

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