The time scale problem in molecular simulations: from transition pathways to reaction coordinates

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Under suitable conditions, first order phase transitions such as the freezing of a liquid or the structural transformation of a solid occur via a nucleation and growth mechanism, in which a nucleus of the stable phase is formed in the metastable phase. The free energetic cost related to the creation of an interface between the two phases prevents this process from occurring rapidly and the transition takes place only if a rare fluctuation produces a nucleus of sufficiently large size. On a molecular time scale, the transition is a rare event and the resulting long time scales present a challenge for computer simulations. Other processes similarly dominated by rare events include chemical reactions, transport in and on solids, as well as protein folding. In this talk, I will first give a general introduction to this topic and then discuss how the transition path sampling methodology provides a framework to address this time scale problem and to study the mechanism and the kinetics of first order phase transformations. As illustrative examples, I will report on our work on the pressure-induced structural transition in Cadmium-Selenide nanocrystals and on the crystallization of a soft sphere fluid. Particular emphasis will be directed towards statistical methods to extract information on the transition mechanism from the simulation data.