From Levinthal's paradox to the enigma of missing structures: Using Minima Hopping to gain insight into potential energy landscapes

Stefan Goedecker
University of Basel (Switzerland)

The number of possible structures of a condensed matter system is growing exponentially with respect the number of atoms in the system. So, for large systems, it is neither in a simulation possible to search over all existing structures to find the geometric ground state structure, nor would it be possible for such a system in nature to find its ground state on any reasonable time scale if it had to visit a large fraction of intermediate structures. This problem has first been noticed in the context of protein folding and is known as the Levinthal paradox. Its solution came also from the protein folding community. The folding of a protein on a short time scale can only be explained if one assumes that the potential energy surface has a funnel like structure that guides the system directly into its ground state without the need to visit a very large number of intermediate structures. The situation is analogous for large molecules, clusters and solids. There is only a realistic chance of finding the ground state structure if the potential energy surface is composed of funnels. Modern structure prediction methods have shed new light on many longstanding structural problems. The structures found by systematic structure prediction simulations for various nano-systems are for instance frequently considerably lower in energy than structures proposed based on chemical/physical intuition. Many systems have a multi-funnel character. In the case of periodic solids, the structures at the bottom of these funnels typically represent different crystalline structures. Even though the number of funnels and therefore the number of possible crystalline structures is typically not huge it turns out that one can find in simulations a considerably larger number of low-energy structures than is known experimentally. I call this fact the enigma of missing structures and I will show what features of the potential energy surface can lead to kinetically inaccessible structures. All the results presented were obtained by a family of methods that are based on the Minima Hopping Method. I will also explain these methods that allow us to find metastable structures, transition states and reaction/transformation pathways on the potential energy surface.