Polymorphs from Phase Transformation Mechanisms – A Kinetic Perspective

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The selection of a given experimental crystal structure is not dictated by thermodynamics alone [1], often kinetic factors play a key role in the formation or preformation structural pattern. In directing these nuclei or pre-nucleation aggregates towards a final product, a more or less efficient kinetic will achieve a certain crystal structure, related to those initial events, which therefore may not corresponds to the lowest energy. Crystal structure prediction protocols often consider a number of low-lying solutions of for example molecular crystal packing, among which the correct solution may be looked for.

While a number of successful stories are being collected and the accuracy of total energy and interatomic force evaluation is increasing, we are just about to start tackling the fundamental question of crystal structures, namely *how they form*. A molecular crystal forms, typically from a solution; a protein fold from a solvated state; a metastable crystal is obtained from a pristine material under changed pressure or temperature.

In this talk, three examples of a kinetic approach to phase transitions will be illustrated:

i) Polymorphism in metallorganic framework compounds, and the determination of ground state and metastable structure from a combination of accelerated molecular dynamics techniques, van der Waals functionals, and calorimetric analysis [2].
ii) Formation mechanisms of novel carbon polymorphs, selection of starting materials and kinetic pathways of formation of distinct structures under varying crystallization conditions [3].
iii) Solid-solid reconstructive phase transitions in elements (allotropes) and inorganic compounds, and the task of determining the free energy of phase transition [4].

Details into crucial steps of phase nucleation and growth, and precise investigation of competing products, and of the reasons for the preference of a certain pathways, are the starting point of a different perspective on materials. Therein, a polymorph is considered with respect to a pathway capable of expressing it, or it is evaluated as a key step towards a different structural motif.

References:

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