ISSUES IN THE AB-INITIO ASSESSMENT OF HCP TRANSITION METALS SELF DIFFUSION

Pasianot, R.C.[1,2,3] and Pérez, R.A.[1,2,3]

[1]*Depto. Materiales, CAC-CNEA, Avda. Gral. Paz 1499, 1650 San Martin*
[2]*CONICET*
[3]*Instituto Sabato, UNSAM / CNEA*

Since about a decade ago, first principles electronic structure techniques have started to impact traditional domains of Materials Science; among the reasons for this are the availability of reliable and efficient codes based on the Density Functional Theory, and the ever increasing power of computing hardware at affordable prices. Notably, under well controlled conditions, these calculations have demonstrated to be as reliable as experiment itself.

A couple of applications of those techniques relevant to the present context include, i) the formation energy of small cell ($\sim$10 atoms) perfect crystals, needed e.g. in the assessment of alloys phase diagrams, and ii) simulations of point defects, situation computationally more delicate and demanding ($\sim$100 atoms), some of which have shed light on fundamental aspects of radiation damage (in bcc metals and Fe in particular).

With the exception of two pioneering works dealing with Si and Na, ab-initio studies on diffusion are of more recent date. Within the framework of Transition State Theory, these do not only involve energetic aspects of the defects but also their vibrational properties. In particular, the literature reports several studies dealing with Al, though only one of them can be considered to be fully self-consistent, that also has resulted in very good agreement with the experimental data.

Following the latter methodology, we use the SIESTA code to tackle the case of hcp transition metals, presently restricted to Zr and Ti. Several issues pertaining to this apparently hard case are commented and analyzed, elements of such a list including i) the suitability of available pseudopotentials, ii) the need to employ fine space grids for the numerical integrations, iii) the need of a rather large basis set, iv) the reliability of the simulation cell size and boundary conditions, etc. All of which impact the precision and convergence of the magnitudes to be evaluated, namely, assuming a standard diffusion mechanism, vacancy formation energy, vacancy formation entropy, and attempt frequency.