Vibrational spectra: from ideal crystals to ideal melts

RAZVAN CARACAS [1,2,3], JEAN-ALEXIS HERNANDEZ [1,4], ZHI LI [1]

1 CNRS, 46 allée d'Italie, Lyon, France
2 Laboratoire de Géologie de Lyon, Ecole Normale Supérieure de Lyon, France
3 CEED, University of Oslo, Norway
4 Ecole Polytechnique, Laboratoire d'Utilisation des Lasers Intenses, Palaiseau, France
* correspondence: razvan.caracas@ens-lyon.fr

Atoms are never fixed. Under the action of external perturbations they move, they vibrate. And this continous state of vibration shapes the thermodynamic behavior of the minerals they build.

Here we show what is hidden behind the vibrational spectrum of a mineral and why we should care about it; how we can relate the macroscopical thermodyamic properties, like heat capacity and free energy to the atomic vibrational spectrum, via the quasiharmonic approximation. Then we will also discuss the limitations of this approach.

But atoms vibrate also in an amorphous systems, like a glass, a superionic conductor, or a melt. Hence we will discuss the peculiarities of the spectra in these systems where the atoms can have both a diffusive and a vibrational component.

A few steps away from the atomic vibrations, a strong connection can be made with the isotope fractionation. This technique is extremely powerful today and allows fast prediction of the isotopic fractionation. We will finish our presentation with a discussion about the extension of this approach to the use of the entire vibrational spectrum to compute the isotope reduced partitioning functions.

Acknowledgements: This research was supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n°681818 – IMPACT). The ab initio simulations were performed on the GENCI supercomputers, under eDARI/CINES grants x106368.