Anharmonic and quantum effects in H-bonded systems with first-principles accuracy

Mariana Rossi

Fritz Haber Institute of the Max Planck Society, Berlin, Germany

In this talk, I will focus on our recent developments for the treatment of anharmonicities and nuclear quantum effects in different classes of H-bonded systems. First, I will discuss our study on molecular crystals, where the complex interplay of subtle effects determine the relative stability of different structures. We estimate all contributions to the free energies of these systems with density-functional theory, including the oft-neglected anharmonic contributions and nuclear quantum effects (NQE), by using a series of different flavors of thermodynamic integration. As an example, for the two most stable forms of paracetamol we find that anharmonic contributions, different descriptions of van der Waals interactions, and nuclear quantum effects all matter to quantitatively determine the stability of different phases [1]. Our studies indicate that anharmonic free energies could play an important role for molecular crystals composed by large molecules and opens the way for a systematic inclusion of these effects in order to obtain a predictive screening of structures. I will then discuss the impact of NQE on the dissociation of water wires on stepped metallic surfaces. The existence of several competing minima at finite temperatures makes the usually reported harmonic approximations of free energy contributions in these systems a questionable approximation. We treat these systems with ab initio path integral molecular dynamics (PIMD) and propose a general scheme based on a space-partition to accelerate PIMD simulations when only physisorption of the adsorbate is involved. We are able to determine that the NQE contributions to free energy differences between intact and dissociated structures are of the order of magnitude of these differences themselves and show how NQE interplay with the electronic structure, changing the average value of work functions by hundreds of meV for the intact system. Finally, I will discuss our most recent efforts in including NQE in dynamical properties like vibrational spectra, which are important for obtaining structural fingerprints that are experimentally also accessible. We present our results from joining colored noise thermostats [2] with thermostatted ring polymer molecular dynamics (TRPMD), which yield sharper peaks and better lineshapes than the original TRPMD implementation.

[1] Rossi, Gasparotto, Ceriotti, Phys. Rev. Lett. 117, 115702 (2016).

[2] Rossi, Kapil, Ceriotti, J. Chem. Phys., accepted (2017).