

Abstract Submitted
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Factors controlling thermodynamic properties at the nanoscale: Ab initio study of Pt nanoparticles¹ GHAZAL SHAFAI, MARISOL ALCANTARA ORTIGOZA, TALAT S. RAHMAN, University of Central Florida — We analyze via density-functional-theory calculations how factors such as size, shape, and hydrogen passivation influence the bond lengths, vibrational density of states (VDOS), and thermodynamic quantities of 0.8-1.7 nm diameter Pt nanoparticles (NPs), whose shape was previously characterized via extended X-ray absorption fine structure spectroscopy (EXAFS) [1]. For a given shape, unsupported NPs display increasingly broader bond-length distributions with decreasing size. Since the VDOS is remarkably non-Debye-like (even for the largest NPs), the VDOS and the thermal properties are not correlated as they are in the bulk. Generally, the fundamental vibrational frequency of a NP is associated with the shape and decreases with increasing size, as in macroscopic systems. Not surprisingly, we find that the frequency of this fundamental mode largely characterizes the thermal properties. We demonstrate that the qualitative difference between the atomic mean-square-displacement and the corresponding mean bond-projected bond-length fluctuations should be taken into account when interpreting the Debye-Waller factor of NPs measured by X-ray (or neutron) scattering or EXAFS. We find that in H-passivated Pt NPs, H desorption with increasing temperature explains the appearance of negative thermal expansion.

[1] B. Roldan Cuenya, et al. (2011), preprint available [Marisol Alcantara Ortigoza](#)
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