Dynamic and static disorder in supported Pt nanoparticles: when static is not static

FD VILA, JJ REHR, U. of Washington, AI FRENKEL, Stony Brook U. — Supported Pt nanoparticles (NPs) exhibit anomalous properties such as negative thermal expansion (NTE) and excessive disorder. Previous finite temperature DFT/MD simulations explain these properties, and show that they arise from bonding heterogeneity both near and far from the support. Pt NPs also exhibit large, so-called “static” or low T disorder, that decreases with increasing size. For small (0.9 nm) NPs, there is significant mean-square bond disorder $\sigma^2$, and a fit to an Einstein model results in an anomalously high Einstein temperature ($T_E = 298 \pm 25$ K vs 179 K in bulk Pt), comparable to Pt-Pt bond strengths in the isolated Pt dimer, as well as an anomalous Gruneisen parameter. To resolve these puzzles, we decompose the $\sigma^2$ obtained from DFT/MD runs into “static”, dynamic, and vibrational components. We find that the anomalous behavior stems from a decrease in the so-called “static” part with increasing temperature, while the vibrational $\sigma^2$ behaves normally with $T_E \approx 179$ K. Finally, we discuss the origin of the pseudo-static $\sigma^2$ and Gruneisen parameter, and their temperature dependence, in terms of zero-frequency behavior.

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Fernando Vila
Univ of Washington

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