Thermal disorder and mechanical anisotropy in nanocrystals

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A strategy to enhance surface properties of nanocrystals is tailoring their bulk crystalline structure. As an example, the performance of metal nanocatalysts is correlated to lattice distortion induced by the mechanical anisotropy of the crystal structure [1]. We demonstrated that the stress caused by interior interfaces in core@shell nanocrystals results in larger lattice deformations than the elemental lattice mismatch [2]. Plasmonic applications push further the interest for a thorough characterization of the influence of the structural anisotropy on the thermal dynamic disorder.

Here we access the thermal disorder in Pd nanocrystals with molecular dynamics simulation. We focus on cubic nanocrystals, which have a particularly pronounced influence of mechanical anisotropy. We find a marked dependence of dynamic disorder on the crystallographic direction that enhances as crystal size decreases (see Fig. 1). 10 nm nanocrystals show a clear separation of the directional-dynamic disorder profiles. Contrary to theoretical models that ignore mechanical anisotropy, the directional profiles deviate from one another starting with the shortest pair distances.

We extracted an analytical model suitable for include the anisotropic thermal disorder we report here within existing analysis methods of both Bragg and PDF powder scattering profiles. Based on experimentally validated atomistic simulations, the model is calibrated with well-known characteristic material properties such as the bulk MSD and structural mechanical anisotropy (i.e., contrast factor). Finally, we used the whole pair distribution function modelling method [3] to test the model against the analysis of powder X-ray diffraction patterns simulated via Debye scattering equation.
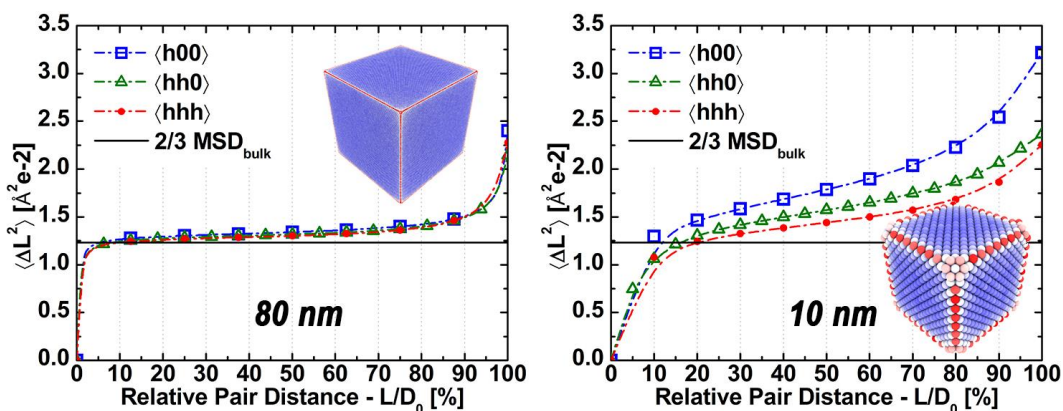

Figure 1. Dependence of the thermal dynamic disorder on the crystallographic direction as a function of the atomic pair distance.

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