Clarifying stability, probability and population in nanoparticle ensembles

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Supplementary Information

The calculations performed in this study were performed from first principles using Density Functional Theory (DFT) within the Generalized–Gradient Approximation (GGA), with the exchange–correlation functional of Perdew-Burke-Ernzerhof (PBE)[1]. This has been implemented via the Vienna Ab initio Simulation Package (VASP)[2,3], which spans reciprocal space with a plane-wave basis, and utilizes an iterative self-consistent scheme to solve the Kohn-Sham equations using an optimized charge-density mixing routine. All calculations were performed using the Projected Augmented Wave (PAW) potentials[4,5], with spin polarisation, to an energy convergence of 10^{-4} eV.The relaxations were performed using an efficient matrix-diagonalization routine based on a sequential band-by-band residual minimization method of single-electron energies[6,7] with direct inversion in the iterative subspace, without symmetry constraints.

All surfaces properties were computed using periodic slabs generated by cleaving a three dimensional (periodic) super-cell along the crystallographic planes of interest, and adding a 15 Å layer of vacuum space. The thickness of each slab varied slightly, depending on the mental and orientation, but was consistently chosen to be between 25Å and 28 Å. In each of these structures, the surfaces were fully relaxed by optimizing the atoms in the 4 outer most atomic layers (the terminal plane, and three further planes beneath), while the atomic planes in the center of the slabs were restricted to the bulk-like atomic positions. This has the advantage of providing more surfaces for analysis (both upper and lower facets), will still constraining the bulk like positions far from the surface.

This method has previously proven successful in describing the temperature-dependent shape, stability and transformation in Ag, Ag, Pd and Pt nanoparticles, and many of these results have been published before.[13–23] They are included here for the sake of convenience.

Since these DFT calculations have been performed at $T \approx 0$, a number of simple expressions have been used here to describe the temperature dependence. Firstly, we have used a semi-empirical expression for determining of $\gamma_i(T)$ proposed by Guggenheim[8]:

$$\gamma_i(T) = \gamma_i(0)\Big(1 - \frac{T}{T_c}\Big)^a, \qquad (1)$$

where a is an empirical parameter (known to be unity for metals[9]) and T_c is the critical temperature at which the structure of the surface deteriorates or changes significantly from the structure in the bulk (is not longer fcc)[10] . The value of T_c is usually taken as the bulk surface melting temperature, but since this has been shown to be size-dependent in metallic nanoparticles[11], the expression of Qi and Wang[12] has also been employed:

$$T_c = T_m\Big(1 - \frac{6r\Omega}{D}\Big) = T_m\Big(1 - qr\Big), \qquad (2)$$

where T_m are the macroscopic surface melting temperatures, D is the average diameter of the nanostructure, r is the atomic radius of platinum, and Ω is a shape dependent factor defined as the ratio of the surface area of the particle divided by the surface area of a sphere of equivalent volume[12]. Since $\sigma = \gamma + A\partial\gamma/\partial A$ the temperature dependence of σ_i has been described in the same way.

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Table 1 Comparison of specific surface energies at $T \approx 0$K, in J/m^2. Original references for relevant metals are included.

Metal	γ_{100}	γ_{110}	γ_{111}	γ_{113}	γ_{120}	γ_{123}	γ_{331}	Details
Ag	0.77	0.86	0.65	0.82	0.80	0.85	0.81	Ref. 20
Au	1.55	1.67	1.34	1.70	1.66	1.71	1.68	Ref. 21
Pd	1.49	1.57	1.29	1.95	1.71	1.80	1.97	Ref. 22
Pt	1.71	1.78	1.26	2.38	2.39	2.30	2.26	Ref. 23

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