Supplementary Information to "Structure and Thermodynamics of Metal Clusters on Atomically Smooth Substrates"

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Structure classification

The atomic-level structure of local minima was characterised using common-neighbour analysis (CNA),[1] with the nearest neighbours defined by a cut-off distance of 3.1 Å. First, the local order around each atom was classified as either icosahedral (IC), face-centred cubic (FC), hexagonal closed-packed (HC), on the surface (SF) as part of a (100) or (111) facet, or ambiguous (X), using the classification criteria of Hendy and Doye.[2] We then characterised the overall cluster morphology, i.e. the *motif*, as either icosahedral (ICO), tetrahedral (TET), decahedral (DEC), face-centred cubic (FCC), hexagonal close-packed (HCP), a combination of the last two (F+H), or otherwise ambiguous (AMB), using a sequence of simple criteria. The motif is classified as ICO if there is an IC atom neighbouring with twelve other IC atoms, and if the total number of IC atoms does not exceed 25 or 37, depending on whether the cluster size (N) is 55 or 147, respectively. Otherwise, if there is an IC atom neighbouring with four other IC atoms, and the total count of IC atoms does not exceed 16 for $N = 55$ (or 22 for $N = 147$), then the motif is classified as TET. Otherwise, if every IC atom is nighbouring at most two other IC atoms, and if the total IC atom count does not exceed 6 for $N = 55$ (or 8 for $N = 147$), then the motif is labelled as DEC. Otherwise, if the number of IC atoms is zero and the combined number of HC and FC atoms exceeds the number of X atoms, then the motif is either FCC if the number of HC atoms is zero, HCP if the number of FC atoms is zero, or else it is labelled F+H. Structures failing to satisfy all these criteria are classified as AMB, which is quite a broad category, often capturing minima that are similar to some from the other (more precisely defined) motifs.

References

(1) (a) Honeycutt, J. D.; Andersen, H. C. Molecular dynamics study of melting and freezing of small Lennard-Jones clusters. *J. Phys. Chem.* **1987**, *91*, 4950–4963; (b) Faken, D.; Jónsson, H. Systematic analysis of local atomic structure combined with 3D computer

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(2) Hendy, S. C.; Doye, J. P. K. Surface-reconstructed icosahedral structures for lead clusters. *Phys. Rev. B* **2002**, *66*, 235402.