Supplementary Information

Reassignment of 'magic numbers' for Au clusters of decahedral and FCC structural motifs

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1 Interpretation of E_{bulk}

For EMT, the energy is defined relative to an FCC crystal (Jacobsen *et al.*, Surf. Sci., 366 (1996) 394). Thus, E_{bulk} is simply zero in that case, as it is the same as the reference system. In our case we use slightly different EMT parameters such that E_{bulk} is not precisely zero but very small (0.0040973 eV). For DFT, the energy of an isolated atom is not zero, therefore E_{bulk} is non-zero. The *absolute* total energy of both the cluster (E_{tot}) and the energy of an atom in the bulk (E_{bulk}) are meaningless but the quantity (E_{tot}-NE_{bulk}) represents the difference in energy between an N atom cluster and N atoms in the crystal, regardless of method using to calculate each of the energetic quantities.

2 Validation of trends with DFT

Three sets of simulations were undertaken using DFT in order to confirm three key results obtained from analysis of the energetics calculated using EMT: 1) a linear interpolation between closed surface endpoint configurations is a good representation for the energy of the intermediate clusters when a (100) surface is opened; 2) the linear interpolation scheme results in too low energy when a (111) surface is opened; 3) a shift in motif preference from Dh to FCC and following back to Dh is observed within a specific size interval.

The evolution of the scaled excess energy, Δ, as either a (100) or a (111) surface is opened is shown in Fig. 1. From these data it appears that the proposed linear interpolation scheme is a valid approximation for the (100) surface at both DFT or EMT level of accuracy. In fact, the linear behavior appears as being more pronounced for the DFT data as compared to the values obtained with EMT. On contrary, when a (111) surface is opened a linear interpolation predicts a too low energy for both DFT and EMT. It is noteworthy that the underestimation is more severe for the DFT data.

A key finding of the present work is that the lowest energy motif shifts frequently from Dh to FCC. An example region where this is apparent is in the size range from 268 to 348 atoms. A zoom on this region is shown in Fig. 2 from which it is clear that Dh is of lowest energy for 268 atoms. A shift to FCC then appears at 290 atoms, which is followed by a shift back to Dh at 325. For this oscillatory trend to be correct, it relies on EMT reliably predicting the relative energies of Dh and FCC clusters. For this reason, we select the three most stable clusters in this region which are: a 268 atom Dh cluster, a 314 atom Oh cluster and a 348 atom Dh cluster. We also consider the most stable open-shell cluster of the opposite motif such that, at each size, there is a Dh and Oh cluster. The EMT and DFT calculated energies of these clusters are collected in Tab. 1. From this it is evident that the osciallatory behavious is captured by both EMT and DFT.

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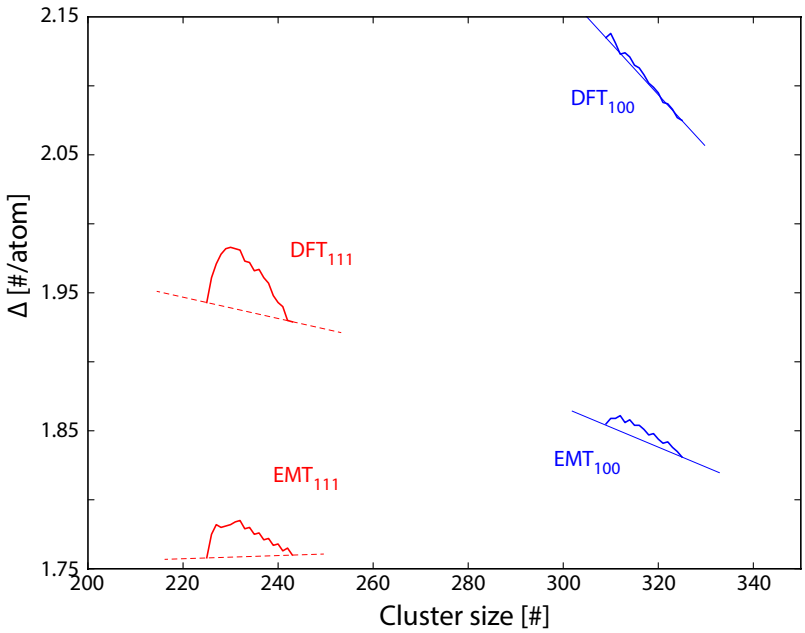

Figure 1: Opening of a (100) and a (111) FCC surface. Blue represents the (100) surface and red (111). From the curves it is clear that for a (100) surface a linear interpolation between the closed shelled end-point configurations is a good approximation for both EMT and DFT. On contrary, for the (111) surface the interpolated energy is significantly lower than the one explicitly determined from a minimization of the cluster.

Table 1: Comparison of scaled excess energy, Δ, when minimized applying either EMT or DFT for the atomic interactions.

Nr atoms	268	314	348
Dh_{EMT}	1.755	1.760	1.755
FCC_{EMT}	1.787	1.739	1.759
Dominant motif	Dh	FCC	Dh
Dh_{DFT}	1.936	1.925	1.859
FCC_{DFT}	1.966	1.908	1.899
Dominant motif	Dh	FCC	Dh

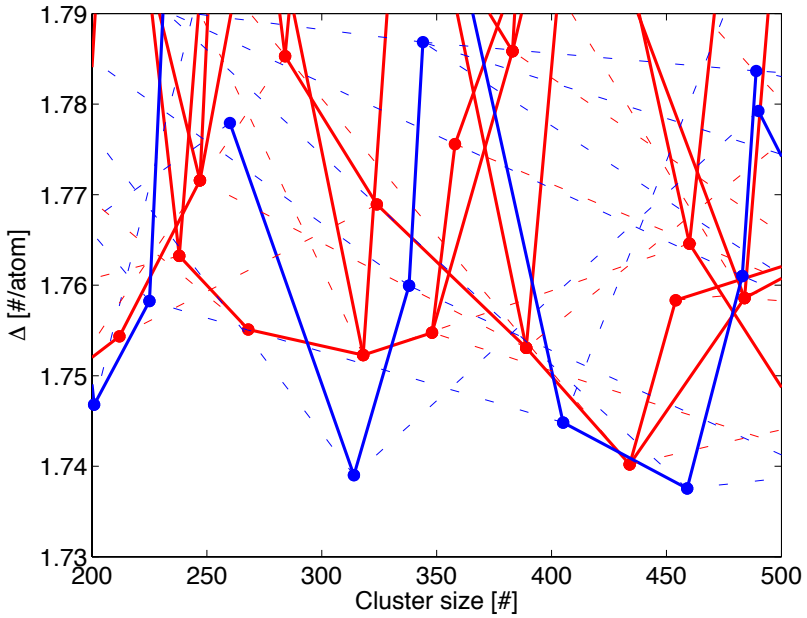

Figure 2: Zoom on interpolated data where a zigzag behavior is observed for the motif preference. Solid (dashed) lines represent 111 (100) surfaces. Red is Dh and blue is FCC. For a 268 atoms cluster the dominant motif is Dh (solid red). At 314 the preferred motif becomes FCC (solid blue). At 348 atoms the Dh motif regains dominance (solid red).

3 Comparison with Wulff construction

The most favourable truncations, j, for a given octahedral corner length, i, which are determined by explicit construction and optimization are compared to those predicted by simple Wulff construction arguments. According to the Wulff criterion, such truncation should fulfill:

$$\frac{\gamma_{(100)}}{\gamma_{(111)}} = \frac{d_{(100)}}{d_{(111)}} \tag{1}$$

where $\gamma_{(100)}$ and $\gamma_{(111)}$ are the energy of a relaxed (100) and (111) surface and $d_{(100)}$ and $d_{(111)}$ are the distances from the center of the (unrelaxed) cluster to the (100) and (111) facets. At the EMT level of accuracy the surface energy for Au is determined to be 0.0569 and 0.0503 eV/Å^2 for the (100) and (111) surfaces, respectively, which yields an energy ratio of 1.13.

The distance ratio $\frac{d_{(100)}}{d_{(111)}}$ for a range of FCC clusters is plotted in Fig. 3. The most favourable truncation for a given i can be identified as the value of j that yields a distance ratio $\frac{d_{(100)}}{d_{(111)}}$ that is closet to the energy ratio (1.13, indicated with a dashed line on Fig. 3). For many of the FCC clusters there is a clearly favourable j, but for others the ideal ratio falls in between the two neighboring and possible cluster sizes, which are assumed to be equally good. The most favourable truncations j for each corner length i are collected in Table 2.

From Table 2 it can be seen that, in general, both the Wulff construction and the explicit optimization yield similar results for the form of the most stable clusters are those where $i = 3j + 1, 2, 3$. Exceptions are found for a couple of smaller clusters ($i = 9, 12$) However, the $i = 9$ case represents a rather small cluster and the Wulff construction is expected to be better for larger clusters. For the other ($i = 12$), there are two truncations that are both quite stable.

Table 2: Most stable truncations (j) for a given octahedral side length (i) of FCC clusters, as determined by Wulff construction and explicit optimization.

Explicit Optimization			Wulff Construction	
# atoms	i	j	i	j
201	7	2	7	2
314	8	2	8	2/3
459	9	2	9	3
586	10	3	10	3
807	11	3	11	3/4
1072	12	3	12	4
1289	13	4	13	4
1654	14	4	14	4/5
2075	15	4/5	15	5
2406	16	5	16	5
2951	17	5	17	5/6
3564	18	5/6	18	6

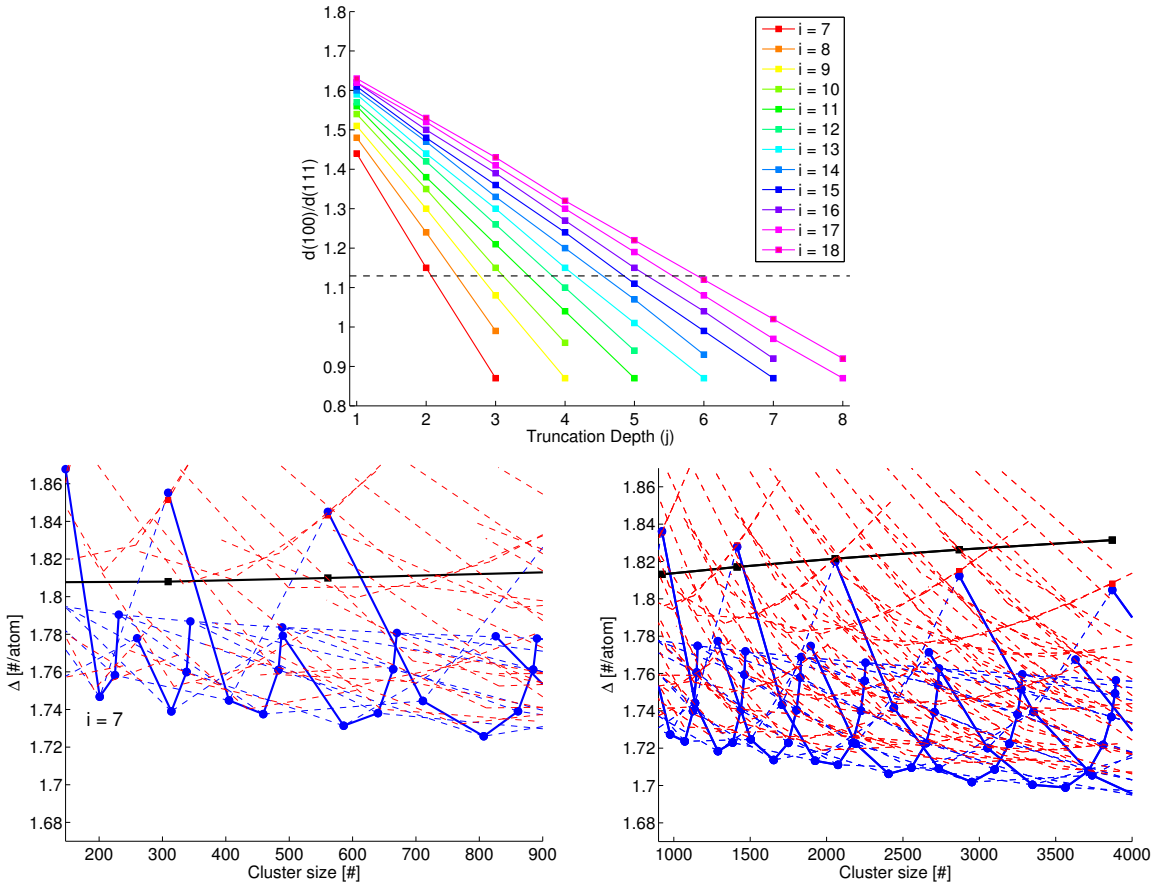

Figure 3: Top: The distance ratio, corner length (i) as a function of truncation depth (j). The dashed line indicates the determined energy ratio, $\frac{\gamma_{(100)}}{\gamma_{(111)}} = 1.13$, as determined using EMT. Bottom: The quantity Δ as a function of size for FCC (red) and FCC (blue) clusters between 150-900 (left) and 900-4000 atoms (right). Solid lines connect FCC clusters of the same edge length (i) of the base octahedron. The smallest group are FCC clusters with i=7 and i increases by 1 for subsequent groups of clusters. Note that all other clusters are drawn with dashed lines for ease of viewing.

4 Vibrational eigenfrequencies

The distribution of vibrational eigenfrequencies is determined for a series of low energy closed shelled clusters for each of the three motifs. The computed eigenvalues are determined within a harmonic approximation and the obtained normalized distributions are shown in Fig. 4. From these figures it is clear that the Ih clusters have a significantly larger contribution of low frequency (low energy) modes as compared to the Dh and FCC clusters. Due to this characteristic, Ih clusters will be entropically favored.

When comparing the distributions for the Dh and FCC clusters the former seems to be slightly dominant at the low frequencies in the first peak ($\leq 3 \times 10^{12}$) while for the second peak ($\geq 3 \times 10^{12}$) neither of the two motifs appear to dominate certain regions. This slight difference gives rise to the increased dominance of Dh clusters at increased temperatures, which is evident in Fig. 4 of the main text.

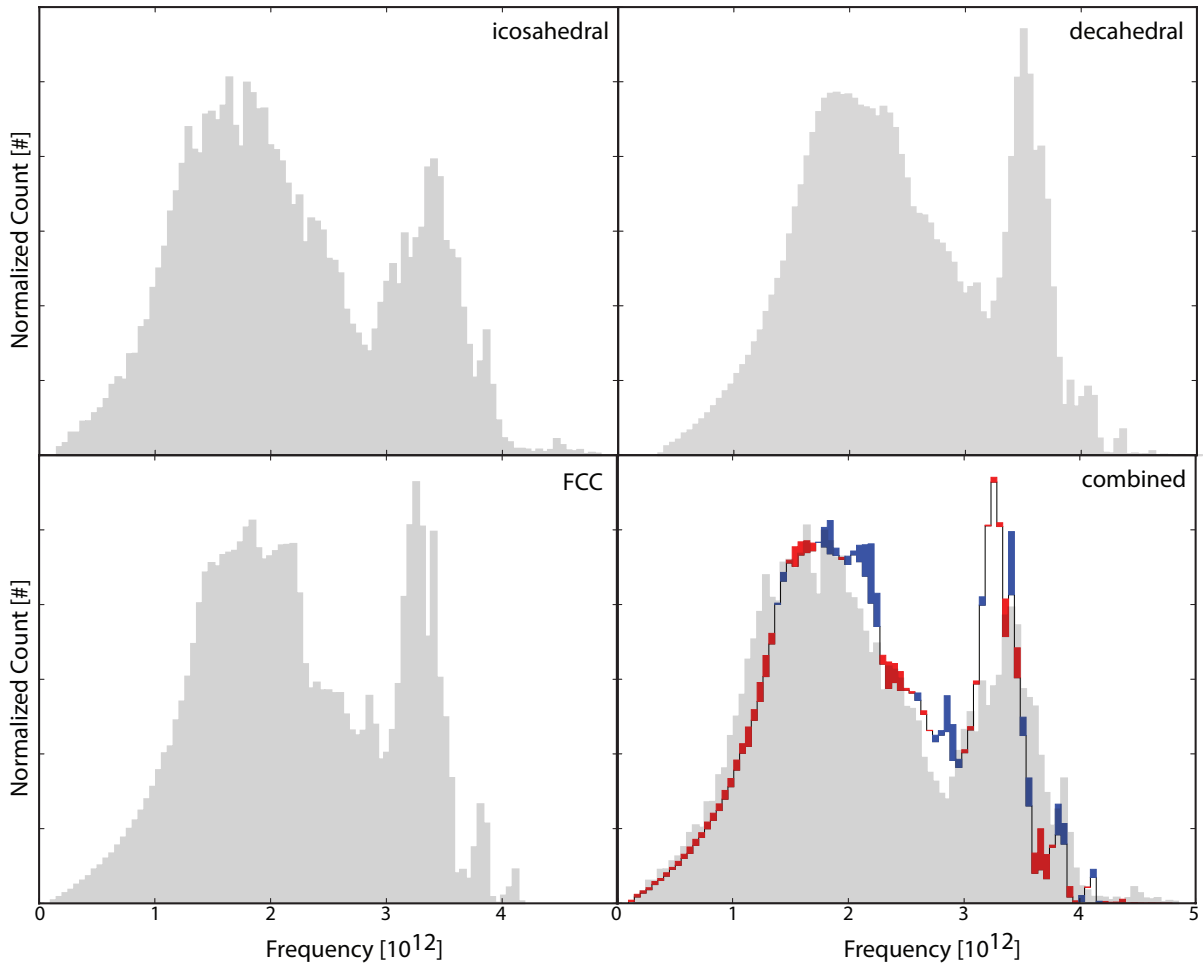

Figure 4: Normalized distribution of eigenfrequencies for a series of closed shelled icosahedral clusters. In the 'combined' panel, grey indicates the icosahedron distribution and black lines indicate the distribution common to both decahedral and FCC clusters. Red indicates regions where the frequency count is higher for decahedral clusters and blue indicates regions where the count is higher for FCC clusters.