SUPPORTING INFORMATION
1.1 Plot of Gupta Potential and Cutoff

Figure 1.1: Plot of the Gupta Potential function, with different parameters and cutoff in each graph for (a) Pd and (b) Au. Black lines represent the parameters of Cleri and Rosato [1], red lines represent the parameters of Baletto et al. [2], and the blue lines show the polynomial cutoff, with $C_s$ and $C_e$ shown by pink and purple dashed lines, respectively.
1.2 Long Range Cut-off in the Gupta Potential

The parameters used in reference [2] incorporate a long distance cut-off into the potential for atoms further than 2 neighbours distance away \((> \sqrt{2}r)\) [3]. The interatomic potential decays with increasing distance and introducing a cut-off speeds up the energy calculations for large clusters.

A 5th order polynomial was introduced, matching that of Baletto et al. [2]. For this, a polynomial replacement for the potential that matches the potential function at the cut-off start \((C_s)\), and is zero at the cut-off end \((C_e)\) is derived. The replacement is applied separately to each exponential component of the Gupta potential. Considering the term:

\[
V_{ij}(r_{ij}) = Ae^{-p(r_{ij}/r_0 - 1)} \quad (1.1)
\]

for \(C_s \leq r_{ij} \leq C_e\) we replace the above expression by the following polynomial \(p_1(r_{ij})\):

\[
V_{ij}^*(r_{ij}) = p_1(r_{ij}) = a_5(r_{ij} - C_e)^5 + a_4(r_{ij} - C_e)^4 + a_3(r_{ij} - C_e)^3 \quad (1.2)
\]

where the coefficients \(a_5, a_4, a_3\) are chosen to match the function and its first and second derivatives for \(r_{ij} = C_s\). For \(r = C_e\), \(p_1(r_{ij}) = 0\). The form of the polynomial ensures that the conditions on the function and its first derivative are automatically matched for \(r_{ij} = C_e\). In the same way, for the term:

\[
\left[ V_{ij}^m(r_{ij}) \right]^{\frac{1}{2}} = \zeta e^{-q(r_{ij}/r_0 - 1)} \quad (1.3)
\]

the following polynomial, \(p_2(r_{ij})\), is used:

\[
\left[ V_{ij}^m(r_{ij}) \right]^{\frac{1}{2}} = p_2(r_{ij}) = x_5(r_{ij} - C_e)^5 + x_4(r_{ij} - C_e)^4 + x_3(r_{ij} - C_e)^3 \quad (1.4)
\]
where the coefficients $x_5$, $x_4$, $x_3$ are calculated to match the form of the Gupta function. The cut-off parameters used are given in Table 1.1, and included in the potential functions plotted in Appendix 1.1.

<table>
<thead>
<tr>
<th>Parameter Set II</th>
<th>Pd</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_s$ (Å)</td>
<td>3.890</td>
<td>4.070</td>
</tr>
<tr>
<td>$C_e$ (Å)</td>
<td>4.764</td>
<td>4.984</td>
</tr>
<tr>
<td>$a_3$</td>
<td>$-5.732 \times 10^{-3}$</td>
<td>$-8.105 \times 10^{-3}$</td>
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<tr>
<td>$a_4$</td>
<td>$-8.477 \times 10^{-3}$</td>
<td>$-1.110 \times 10^{-2}$</td>
</tr>
<tr>
<td>$a_5$</td>
<td>$-5.723 \times 10^{-3}$</td>
<td>$-6.828 \times 10^{-3}$</td>
</tr>
<tr>
<td>$x_3$</td>
<td>-3.131</td>
<td>-2.232</td>
</tr>
<tr>
<td>$x_4$</td>
<td>-4.861</td>
<td>-3.258</td>
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<tr>
<td>$x_5$</td>
<td>-2.157</td>
<td>-1.383</td>
</tr>
</tbody>
</table>

Table 1.1: Cut-offs and polynomial coefficients used for Au and Pd (to 4 significant figures) for parameter set $II$
1.3 Energetic Analysis

1.3.1 Pd\textsubscript{N} Clusters

12-Vertex Structures: Icosahedra, Ino-Decahedra and Cuboctahedra.

Figure 1.2: Left: Plot of $E_b$ for Pd\textsubscript{N} structures against $N$. Solid lines represent the parameter set $I$ of Cleri and Rosato [1], and dashed lines represent the parameter set $II$ of Baletto et al. [2]. Right: Plot of $E_b$ for Pd\textsubscript{N} structures against $N^{-\frac{1}{3}}$. Ih (black squares), I-Dh (red circles) and CO (blue triangles) are shown in both plots; $E_{coh}$ of 3.89 eV [4]) is displayed as a grey solid line.

Figure 1.2 plots $E_b$ for Ih, I-Dh and CO structures, with increasing shell sizes $k$, against $N$. For $N < 100$, $E_b$ rapidly increases, before levelling off as $N > 500$; this trend is consistent for both parameter sets. Identification between the different structural motifs is energetically difficult, implying that they are all closely competitive in energy at this size. A spacing between trend lines is visible for the two parameter sets: parameter set $I$ rises to a higher level than parameter set $II$, before flattening out asymptotically relative to $E_{coh}$. The difference in gradients between parameter sets $I$ and $II$ can be identified in the right of Figure 1.2 where an approximation to the $E_{coh}$ is achieved for $N^{-\frac{1}{3}} \to 0$ when $N^{-\frac{1}{3}}$ is plotted against $E_b$. Linear extrapolation to 0 for parameter set $I$ gives a slightly over-exaggerated $E_{coh}$ (3.92 eV) compared to the experimentally measured value.
(3.89 eV [4]), whilst parameter set II offers better agreement to this measurement (3.88 eV).

1.3.2 Au\textsubscript{N} Clusters

12-Vertex Structures: Icosahedra, Ino-Decahedra and Cuboctahedra.

Figure 1.3: Main: Plot of $E_b$ for Au\textsubscript{N} structures against $N$. Solid lines represent the parameter set I of Cleri and Rosato [1], and dashed lines represent the parameter set II of Baletto et al. [2]. Inset: Plot of $E_b$ for Au\textsubscript{N} structures against $N^{-\frac{1}{3}}$. Ih (black squares), I-Dh (red circles) and CO (blue triangles) are shown in both plots; the bulk $E_{coh}$ (3.81 eV [4]) is displayed as a grey solid line.

Figure 1.3 compares $E_b$ for the high-symmetry Au\textsubscript{N} structures of the Ih, I-Dh and CO geometries. Similar trends to the results of Pd\textsubscript{N} are seen with sharply increasing $E_b$ for $N < 100$, levelling out asymptotically towards the bulk $E_{coh}$ value of 3.81 eV [4] as
$N \to \infty$. Parameter set II tends to a higher value of $E_b$ than parameter set I, an inverse of the results for Pd$_N$ clusters (Figure 1.2). Attention to the inset, which relates $E_b$ to the bulk limit ($N^{-\frac{1}{3}} \to 0$), suggests that the parameter set I underestimates the extrapolated bulk $E_{coh}$ value (3.77 eV), whilst parameter set II does not (3.81 eV).

Structural preferences are difficult to identify in Figure 1.3; we can calculate relative stabilities ($\Delta E_b$) of different geometries with identical nuclearities using:

$$\Delta E_b = E_{b_{Ih}} - E_{b_x}$$

(1.5)

where the binding energies of I-Dh or CO can be directly compared with Ih ($E_{b_{Ih}}$) when substituted in for $E_{b_x}$. Positive values indicate reduced stability, and a negative value indicates increased stability, relative to the Ih; thus $\Delta E_b$ is plotted in Figure 1.4 for Au$_N$ clusters.

For parameter set I we see intersection of $E_{b_{Ih}}$ at $N = 682$ by $\Delta E_{b_{I-Dh}}$ and at $N = 923$ by $\Delta E_{b_{CO}}$, calculated using a linear fit. For parameter set II these intersections of $E_{b_{Ih}}$ are at lower $N$: 284 and 393 for $\Delta E_{b_{I-Dh}}$ and $\Delta E_{b_{CO}}$, respectively. The values of $N$ for these intersections are much less than found for Pd$_N$, implying relative instability of the close-packed cluster geometries (Ih, I-Dh) with respect to the crystalline bulk fragments for Au nanoparticles.
Figure 1.4: Plot of $\Delta E_b$ for Ih (black), I-Dh (red) and CO (blue) Au$_N$ structures against $N$. Solid lines represent parameter set $I$ of Cleri and Rosato [1], and dashed lines represent parameter set $II$ of Baletto et al. [2].
1.3.3  \((\text{Pd}_{\text{core}}\text{Au}_{\text{shell}})_N\) Clusters

Figure 1.5: Plots of \(\Delta\) against \(N\) for the \(\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}\) 12-vertex high-symmetry structures (solid lines), using parameter set \(I\) of Cleri and Rosato [1], with cores: (a) Pd\(_1\) (b) Pd\(_{13}\) (c) Pd\(_{55}\) (d) Au\(_{147}\). Ih (black squares), I-Dh (red circles) and CO (blue triangles) are shown, with Au\(_N\) (dashed lines) also plotted.
LIST OF REFERENCES


