THERMAL PROPERTIES AND GROUND-STATE STRUCTURES OF PURE AND ALLOY NANOCLUSTERS VIA MOLECULAR DYNAMICS SIMULATION

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THERMAL PROPERTIES AND GROUND-STATE STRUCTURES OF PURE AND ALLOY NANOCCLUSTERS VIA MOLECULAR DYNAMICS SIMULATION

by

ONG YEE PIN

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<td>BCGA</td>
<td>Birmingham Clusters Genetic Algorithm</td>
</tr>
<tr>
<td>BH</td>
<td>Basin Hopping</td>
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<td>BTIMD</td>
<td>Brownian Type Isothermal Molecular Dynamics</td>
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<td>CCM</td>
<td>Atom Closest to the Centre of Mass</td>
</tr>
<tr>
<td>CCS</td>
<td>Cubic Coupling Scheme</td>
</tr>
<tr>
<td>COM</td>
<td>Centre of Mass</td>
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<tr>
<td>FCM</td>
<td>Atom Farthest from the Centre of Mass</td>
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<td>FTF</td>
<td>Atom Farthest to Atom Farthest from the Centre of Mass</td>
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<tr>
<td>GA</td>
<td>Genetic Algorithm</td>
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<td>MBH</td>
<td>Multicanonical Basin Hopping</td>
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<td>MD</td>
<td>Molecular Dynamics</td>
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<td>PES</td>
<td>Potential Energy Surface</td>
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<td>PTMBHGA</td>
<td>Parallel Tempering Multi-Canonical Basin Hopping plus Genetic Algorithm</td>
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<td>RMS</td>
<td>Root-mean-square</td>
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<td>USR</td>
<td>Ultrafast Shape Recognition</td>
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<td>VMD</td>
<td>Visual Molecular Dynamics</td>
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LIST OF SYMBOLS

\( n \)  
Cluster size, or number of atoms

\( T \)  
Temperature

\( N p_{A,B} \)  
Number of homotops

\( A_{ij} \)  
Coefficient of repulsive pair term

\( \xi_{ij} \)  
Effective hopping integral between \( i \) and \( j \)

\( p_{ij} \)  
Dependence on the repulsive interatomic distance between \( i \) and \( j \)

\( q_{ij} \)  
Dependence on the attractive interatomic distance between \( i \) and \( j \)

\( r_{ij}^{(0)} \)  
Equilibrium first neighbour distance

\( f_i \)  
Fitness value of candidates cluster \( i \)

\( V_{\text{max}} \)  
Maximum energy cluster in the population

\( V_{\text{min}} \)  
Minimum energy cluster in the population

\( V(x) \)  
Potential energy

\( V_i \)  
Potential energy of \( i \)th atom

\( V_h \)  
Highest potential energy

\( V_l \)  
Lowest potential energy

\( E_{\text{old}}, E_{\text{new}} \)  
Local minimum energy
\( \tilde{E}(X) \) Transformed energy topology

\( \beta \) Confidence level

\( w_{mu} \) The non-Boltzmann multicanonical weight factor

\( \beta^m (\tilde{E}) \) Effective inverse temperature

\( \alpha^m (\tilde{E}) \) Multicanonical parameter

\( x_{i(a)} \cdot x_{i(b)} \) x-component position coordinate

\( p_{i(a)x} \cdot p_{i(b)x} \) x-component momentum

\( E_n \) Potential energy defined from the Gupta many-body potential

\( \mu_{a,x} \cdot \nu_{a,x} \cdot \eta_{a,x} \) Spherical Gaussian as a function of vector position \( r_i \) of atom \( i \)

\( p_{0,a} \) Average thermal momentum

\( d_0 \) Dimensionless constant

\( L_0 \) Constant with dimension of length

\( e_{0,a} \) Energy constant

\( \omega_D \) Debye frequency

\( \Delta t \) Time step

\( \zeta \) Shape similarity index

\( m \) Total number of statistical moment descriptors
$\Delta_2E$ Second energy difference

$C_v$ Specific heat

$\delta$ Lindemnn index

$r_{ij}$ Relative bond length

$P(\zeta)$ Probability distribution function of shape similarity index
SIFAT-SIFAT TERMA DAN STRUKTUR KEADAAN ASAS
NANOKLUSTER TULEN DAN PANCALOGAM MELALUI SIMULASI
DINAMIK MOLEKUL

ABSTRAK

Dalam bidang fizik komputasi, sifat terma nanokluster adalah antara topik yang biasa dikaji melalui simulasi dinamik molekul. Walau bagaimanapun, kaedah pasca-proses data dan penentuan julat pra-pencairan serta peleburan nanokluster pada komposisi tertentu adalah berbeza bagi setiap penyelidikan. Dalam tesis ini, kajian mengenai sifat terma bermula dengan memperoleh struktur keadaan dasar nanokluster emas-platinum 38-atom \( \text{Au}_n\text{Pt}_{38-n} \) bagi pelbagai komposisi (di mana \( 0 \leq n \leq 38 \)) dengan menggunakan algoritma *Parallel Tempering Multicanonical Basin Hopping plus Genetic Algorithm* (PTMBHGA). Nanokluster dwilogam \( \text{Au}_{32}\text{Pt}_6 \) dengan simetri \( D_{6h} \) telah dipilih untuk perincian lanjutan sifat-sifat termanya memandangkan ia merupakan nanokluster dwilogam yang paling stabil dalam tesis ini. Kod dinamik molekul yang dikenali sebagai *Brownian type isothermal molecular dynamics* (BTIMD). Haba tentu, \( C_v \) dan indeks Lindemann, \( \delta \) yang merupakan penghurai-penghurai yang lazim dalam memantau kelakuan peleburan nanokluster telah dikira untuk \( \text{Au}_{32}\text{Pt}_6 \). Lengkungan \( C_v \) yang diperolehi menunjukkan bahawa peleburan nanokluster ini berlaku di antara \( T = 1000 \text{ K} \) dan \( 1050 \text{ K} \). Kewujudan fasa pra-peleburan dalam kalangan nanokluster telah dibuktikan melalui lengkungan \( C_v \) dan \( \delta \) yang menunjukkan peningkatan secara mendadak pada \( T = 700 \text{ K} \) sehingga \( T = 800 \text{ K} \). Kod *Ultrafast Shape Recognition* (USR) telah diperkenalkan untuk memperinci fenomena pra-peleburan. Data yang terkumpul diplotkan dalam bentuk jarak atom dan fungsi taburan kebarangkalian bagi indeks keserupaan bentuk.
Kedua-dua hasil kajian tersebut telah megesahkan secara berdikari bahawa pra-peleburan berlaku di antara \( T = 760 \) K dan 770 K. Berbagaibagai pendekatan komputasi yang dicuba di dalam tesis ini memeperlihatkan keputusan-keputusan yang tertumpu untuk julat pra-peleburan dan peleburan nanokluster-nanokluster yang dikaji. Di antara kaedah-kaedah tersebut, pendekatan USR yang memerlihatkan keputusan yang terperinci terhadap kelakuan peleburan nanokluster. Kaedah ini telah membuktikan ia sendiri sebagai penghurai yang lebih tepat berbanding dengan haba tentu, \( C_v \) dan indeks Lindemann, \( \delta \).
THERMAL PROPERTIES AND GROUND-STATE STRUCTURES OF PURE AND ALLOY NANOCLUSTERS VIA MOLECULAR DYNAMICS SIMULATION

ABSTRACT

The study of thermal properties of nanoclusters via molecular dynamics simulation is a common research topic in computational physics. However, the methods of post-processing and determining the pre-melting and melting range of nanoclusters at specific composition differ in every research. In this thesis, the study of thermal properties was started by obtaining the ground-state structure of 38-atoms gold-platinum nanoclusters $Au_nPt_{38-n}$ of various composition (where $n = 0,1,...,38$) using Parallel Tempering Multicanonical Basin Hopping plus Genetic Algorithm (PTMBHGA). Bimetallic nanocluster $Au_{32}Pt_6$ with D$_{6h}$ symmetry has been selected for further investigation in the thermal properties, as it is the most stable bimetallic nanocluster studied in this thesis. To study the melting mechanism of the clusters, a molecular dynamics code known as Brownian type isothermal molecular dynamics (BTIMD) was used. Specific heat, $C_v$ and Lindemann index, $\delta$, which are the common descriptors used to monitor the melting behaviour of clusters were calculated for $Au_{32}Pt_6$. The $C_v$ curve revealed that the melting of this nanocluster commenced between $T = 1000$ K and $1050$ K. Both $C_v$ and $\delta$ curves showed drastic increase at $T = 700$ K to $T = 800$ K, indicating the presence of pre-melting phase in nanoclusters. To scrutinize the pre-melting phenomena, ultrafast shape recognition (USR) code has been introduced. The data was plotted into atomic-distance plots and probability distribution function of shape similarity index. Both these two results independently proved that the pre-melting stage occurred between $T = 760$ K and 770 K. Various independent computational methods attempted in this thesis shown
convergent results in the pre-melting and melting range of the studied nanoclusters.

Amongst these methods, the USR approach provided the most detailed insight to the melting behaviour of the nanoclusters. It has proven itself to be a more precise as indicator compared to specific heat, $C_v$ and Lindemann index, $\delta$. 
CHAPTER 1

INTRODUCTION

The size of an atom ranges from $1 \times 10^{-10}$ m to $5 \times 10^{-10}$ m, which is about 0.1 to 0.5 nanometre. When few or more atoms group together, they form a minute atomic structure which is about the size of a nanometre. Due to the advancement of nanotechnology, these atomic structures have been studied extensively. In this thesis, thermal properties of atomic lattices in the nanometric scale are studied. These atomic lattices will then be regarded as “nanoclusters”.

1.1 Nanoclusters

Nanocluster is a group of particles (atoms or molecules) with its size in the order of nanometre ($10^{-9}$ m) formed by any countable number of atoms (2 to 10n, where n can be up to 6 or 7) (Johnston 2002, pp. 25) that are combined together (Logsdail 2011, pp. 2). Nanoclusters can be formed from identical atoms (homo-atomic) or two or more types of atoms (hetero-atomic). An example of homo-atomic nanoclusters is platinum nanocluster, Pt (Saxena et al. 2011). A good example of hetero-atomic nanocluster is silicon carbon nanocluster, SiC (Pradhan et al. 2004). Each type of clusters has their own uniqueness that make them a worthwhile topic to study.
Nanoclusters can also be classified according to the types of element from which the clusters are comprised of. The classification includes metallic nanoclusters (metallic elements), semiconductor nanoclusters (carbon, silicon and germanium), ionic nanoclusters (elements that involve ionic or electrostatic bonding), rare gas nanoclusters (elements from helium to radon in group 18), molecular nanoclusters (formed from supersonic expansion of molecular vapour) and nanocluster molecules (inorganic and organometallic nanoclusters). The clusters to be studied in this thesis are specific types of metallic nanoclusters. Metallic clusters are formed by elements with metallic bonding, which includes the simple s-block alkali and alkaline earth metals (from group 1 and 2 in periodic table) and transition metals with valance d orbitals (Johnston 2002, pp. 26).

Due to high surface area to volume ratio in nanoclusters, their physical properties generally display a size-dependence behaviour. The surface energy contribution is playing an important role in the study of nanoclusters (Baletto et al. 2005). As a result, nanoclusters of different sizes will exhibit different properties despite being formed by the same elements.

1.2 Importance of Nanoclusters

The increasing interest in nanoclusters throughout the past decades is due to the possibilities of them having distinct physical and chemical properties compared to bulk state (Ferrando et al. 2008). The potential applications of nanocluster technology in physics, chemistry, biology, medicine and our daily life have accelerated the progress of research on nanoclusters. The application of nanocatalysis in industry, hydrogen storage and high sensitivity magnetic sensors have become the
factors that drive researchers to study further into nanoclusters (Carabineiro et al. 2007) (Van Dijk 2011, pp. 3). The research community has been attracted by its ability to control the chemical reactivity and physical properties of nanoclusters to form new materials that can be tailored according to the requirements in industrial applications.

To understand the properties of nanoclusters, researchers have searched for the most stable structures with the lowest potential energy (Baletto et al. 2005). After finding the geometrical and electronic structure of nanoclusters, the results will be branched out to the studies of catalytic, magnetic, optical and thermal properties. Due to the limitation in current technology, the bare cluster without encapsulation is not stable and most of the time it has to be concealed with ligands. Since the properties of the nanoclusters are not easily measured in experiments, theoretical studies and computational methods have become important tools in development and application of nanocluster (Johnston 2002, pp. 29).

Most of the single element nanoclusters in periodic table had been studied widely. Motivated by the interest to fabricate intermetallic materials used in catalysis, engineering and electronics, bimetallic and trimetallic nanoclusters with the flexibility to control the structure and properties have drawn widespread interest among researchers (Ferrando et al. 2008). The range of properties for bimetallic and trimetallic nanoclusters can be widely enhance by tuning the size, atomic ordering and compositions. The structures obtained from bimetallic nanoclusters can differ from pure nanoclusters with the same number of atoms, hence some bimetallic nanoclusters with magic size and compositions will possess strong stability.
From theoretical point of view, the idea of “homotops” have been introduced to describe the isomers of bimetallic nanocluster $A_xB_y$ with fixed number of atoms ($N = x + y$) and composition ($x/y$ ratio) which have identical geometrical arrangement but with A and B types of atoms arranged differently (Jellinek et al. 1996). A geometrical isomer of $N$-atom $A_xB_y$ nanocluster will generate $NP_{A,B}$ homotops, where

$$NP_{A,B} = \frac{N!}{N_A!N_B!} = \frac{N!}{N_A!(N-N_A)!} \quad (1.1)$$

$N$ is the total number of atoms, $N_A$ and $N_B$ are the number of atoms of type A and type B respectively. From Equation (1.1), $NP_{A,B}$ rises rapidly with the increase of $N$. As a consequence, the global optimization process to study bimetallic nanoclusters becomes increasingly complicated (Ferrando et al. 2008).

### 1.3 Gold-Platinum Nanoclusters

Gold (Au) with a filled d-orbital and atomic number 79 is a material which has been studied intensively due to its unique capability to hold as planar structure from 3 to 14 atoms in gold nanoclusters (Xiao et al. 2004a). Moreover, gold nanoclusters are relatively stable in acidic and alkaline solution (Tang et al. 2009).

The stability of gold makes it unreactive in bulk form. However, it can become reactive in the form of a nanocluster. With the ability to resist bacterial infection, gold nanoclusters are widely used in medical field, including the microsurgery of ears and other surgery that require implants with the risk of infection (Giasuddin et al. 2012). Besides, gold nanoclusters serve as catalyst in the electrocatalytic oxidation of carbon monoxide (CO) in industry (Maye et al. 2000).
Meanwhile, platinum (Pt) is a transition element in periodic table with atomic number 78. It is an important catalyst in various industries, including part of catalyst in automotive catalytic converters to diminish toxic pollutants (Xiao et al. 2004b), oxygen reduction and polymer electrolyte membrane fuel cell (Tang et al. 2009). However, researcher are searching for a better alternative to reduce the involvement of platinum due to its limited supply, high cost and susceptibility to poisoning from oxidation products (Tang et al. 2009).

Gold-platinum nanoclusters are widely used in industrial as effective catalyst in oxygen reduction process (Wanjala et al. 2010) and fuel cell electrocatalysis (Maye et al. 2004). Furthermore, they have been investigated for methanol and CO electrooxidation (Piotrowski et al. 2012). The structures of gold-platinum nanoclusters have been investigated while the results show that they are immiscible in bulk form but experimentally proven that they can exist as nanoclusters (Mott et al. 2007).

1.4 Objective of Study

1. As clusters consist of gold and/or platinum are widely used in industries, it becomes an essential piece of information as what are the temperatures at which gold nanoclusters undergo structural changes. In order to know how gold-platinum nanoclusters are affected by temperature variation, we shall study their possible structures at high temperatures, as they are altered, as well as the melting behaviour of these nanoclusters.
2. In order to study the thermal properties of gold platinum nanoclusters of choice, their stable structures, or lowest-energy states, have to be identified. Several compositions of bimetallic gold platinum nanoclusters have been studied in the literature, including those with 40 (Leppert et al. 2011) and 55 atoms (Bochicchio et al. 2013).

3. Conventional methodologies to study thermal instabilities of nanoclusters, such as Lindemann index and specific heat capacity curve, turn out to be not sufficiently sensitive to capture the melting behavior during the pre-melting phases. Quantifying the melting behaviour of nanoclusters during pre-melting phases is essential to understand the changes that occur within the nanocluster as temperature varies. In the thesis, a novel approach is proposed to quantify and capture these details.
CHAPTER 2

THEORETICAL BACKGROUND AND METHODOLOGIES

The main issue this thesis wishes to address is about the structural and thermal behaviour of gold-platinum clusters. To this end, a specific global optimization search algorithm named Parallel Tempering Multicanonical Basin Hopping plus Genetic Algorithm (PTMBHGA), is used to generate the ground state structure of a given atom composition starting from a random configuration. Once the clusters with minimal energies have been obtained as an end output from a completed PTMBHGA run, they will be subjected to molecular dynamics (MD) thermal evolution. The specific MD algorithm used is known as Brownian type isothermal molecular dynamics simulation. The energy calculator used to calculate the potential energy of the atomic configurations generated during the process of global minimum search in the PTMBHGA algorithm, which is also the same as that used in the MD simulation, is the Gupta potential. The MD evolution using a purpose-specific numerical algorithm known as ultrafast shape recognition. It is meant to abstract in a frame-by-frame manner information of the atomic configurations so that the detailed mechanism of the melting procedures occurring during the thermal evolution of the system can be statistically quantified. The overall flow of the calculation procedure is shown in the flow chart in Figure 2.1.
The main components of the calculation procedure in the flow chart are explained in the following subsections.

2.1 Parallel Tempering Multicanonical Basin Hopping Plus Genetic Algorithm (PTMBHGA)

The first step in the theoretical study of a nanocluster is to identify its ground-state structure which is, by definition, its lowest energy state. Identification of ground-state structure is the first most important task before one can advance into calculating the physical properties of a cluster. In principle, all measurable observables of a nanoclusters can be derived theoretically if its ground state is known. Semi-empirical methods such genetic algorithm and basin hopping, which work as global energy optimizers, are commonly used in the search for ground-state structure. As an example, Birmingham Clusters Genetic Algorithm (BCGA) is a genetic algorithm developed by R.L. Johnston as global minimum search algorithm (Johnston 2003). BCGA have been applied in various studies from ionic clusters, metal clusters to bimetallic clusters, such as CuAu nanoclusters (Darby et al. 2002) and PdPt nanoclusters (Massen et al. 2002). Another global minimal search algorithm to mention here is Parallel Tempering Multicanonical Basin Hopping plus
Genetic Algorithm (PTMBHGA) (Hsu et al. 2006). The latter will be used in this thesis as the global minimum searching tool.

Parallel Tempering Multicanonical Basin Hopping plus Genetic Algorithm (PTMBHGA) is a software package developed by the Complex Liquid Lab in the National Central University, Taiwan (Hsu et al. 2006). PTMBHGA was designed to compute the lowest energy geometries (ground-state structures) of bimetallic nanoclusters. Their searching technique combines both basin hopping and genetic algorithm, and is claimed to improve the potential energy surface (PES) search and resolve the issue of calculations being trapped in local minima.

2.1.1 Gupta Many Body Potential

In order to calculate the interactions between many-body atoms, n-body Gupta potential is employed. The empirical potential is written as:

$$E_n = \sum_{i=1}^{n} \left\{ \sum_{j=1}^{n} A_{ij} \exp \left( -p_{ij} \left( \frac{r_{ij}(0)}{r_{ij}^{(0)}} - 1 \right) \right) - \left[ \sum_{j=1}^{n} \xi_{ij}^{2} \exp \left( -2q_{ij} \left( \frac{r_{ij}(0)}{r_{ij}^{(0)}} - 1 \right) \right) \right]^{1/2} \right\}$$

(2.1)

$A_{ij}$, $\xi_{ij}$, $p_{ij}$, $q_{ij}$ and $r_{ij}^{(0)}$ are parameters fitted to bulk quantified data by Cleri and Rosato for cohesive energy, lattice constant and elastic constant for face centred cubic crystal structure at 0 K (Cleri et al. 1993). $A_{ij}$ is coefficient of repulsive pair term, $\xi_{ij}$ is the effective hopping integral between $i$ and $j$, $p_{ij}$ and $q_{ij}$ describe the dependence on the repulsive and attractive interatomic distance between $i$ and $j$, and $r_{ij}^{(0)}$ is the equilibrium first neighbour distance.
The parameters used in this work, including those for gold atoms (Au-Au), platinum atoms (Pt-Pt) and gold platinum atoms (Au-Pt), are listed in Table 2.1.

Table 2.1: Gupta parameters for gold, platinum and gold platinum atoms.

<table>
<thead>
<tr>
<th></th>
<th>p</th>
<th>q</th>
<th>A(eV)</th>
<th>ξ(eV)</th>
<th>r₀(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Au</td>
<td>12.229</td>
<td>4.036</td>
<td>0.2061</td>
<td>1.79</td>
<td>2.884</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>10.621</td>
<td>4.004</td>
<td>0.2795</td>
<td>2.695</td>
<td>2.7747</td>
</tr>
<tr>
<td>Au-Pt</td>
<td>10.42</td>
<td>4.02</td>
<td>0.25</td>
<td>2.2</td>
<td>2.8294</td>
</tr>
</tbody>
</table>

2.1.2 Genetic Algorithm

Genetic algorithm (GA) is a global minimum search algorithm developed from the inspiration of evolution process. It was first used in the 1970s by John Holland from University of Michigan (Borbón 2011). He proposed four basic elements for a generic GA algorithm, namely, encoding scheme, fitness function, selection methods and lastly the genetic operator (Yen 2015).

The particular flavour of GA as implemented in the PTMBHGA code follows the scheme as described below. The process starts from encoding a three dimensional coordinates of initial population \((x, y, z)\) into one dimensional coordinates \((X_1, X_2, \ldots, X_i)\), with \(i = 3 \times \) the number of atoms of the initial population. It is then followed by the calculation of the potential energy using Gupta potential and the computation of local minima using conjugate gradient minimization (L-BFGS) method. The local minima obtained will then undergo the fitness evaluation (for certain populations) using the equation:

\[
F_i = \frac{(V_{max} - V_i)}{(V_{max} - V_{min})} \quad (2.2)
\]

\[
f_i = \frac{F_i}{\sum_{j=1}^{20} F_j} \quad (2.3)
\]
where $V_{max}$ and $V_{min}$ are the maximum and minimum energy cluster in the population and $f_i$ is the normalized fitness. The statistics obtained are used in the formation of “children” (next generation) of the GA calculations. 75% of the “parents” individuals will be retained for the creation of next generation individuals. The “parents” individuals with higher fitness will undergo five genetic operators which include inversion, arithmetic mean, geometric mean, n-point crossover and 2-point crossover to sort out the “children” individuals (Lai et al. 2002).

The GA process is repeated until it fulfils either one of the criterion, which is, the potential energies obtained remains unchanged for a few steps, or, the simulations end with the steps fixed at the beginning of the GA process configurations.
Figure 2.2: Flow chart of genetic algorithm in PTMBHGA.

- Start
- Initialize a population of 20 individuals
- Transform 3-dimensional coordinates of initial populations into 1-dimension
- Calculate the potential energy for all individuals using Gupta potential
- Obtain the local minima of all individuals using conjugate gradient minimization, L-BFGS
- Evaluate the normalized fitness for local minima
- Discard 25% of the “parents” individuals with lower fitness
- ¼ of the retained “parents” individuals (randomly selected) undergo five genetic operators process to form the “children” individuals
- Calculate the local minima for the “children” individuals and add into the group of “parents” individuals
- Check if 7 or more “parents” individuals have the same potential energy
  - Yes: Output global minimum energy
  - No: Continue with the flow chart
2.1.3 Basin Hopping

Basin hopping is a potential energy surface analysis which searches for a global minimum across the potential energy landscape of a system formed by a lot of local minima (Zhan et al. 2004). This algorithm was proposed in 1997 by Wales and Doye to locate the global minimum structure for Lennard-Jones Clusters up to 110 atoms (Wales et al. 1997).

The end results of the potential energy surface analysis can be represented by the following equation:

$$\tilde{V}(X) = \min\{V(x)\}$$ \quad (2.4)

where \textit{min} denote the local-energy minimization and \(V(x)\) represents the potential energy (Lai et al. 2002).

In the basin hoping algorithm, an initial random arrangement of the nanocluster is calculated numerically to obtain the local minimum energy of the nanocluster. The simulation starts with the calculation of the local minimum energy for the initial random coordinate generated. The local minimum energy, \(E_{old}\) obtained is then fit into equation:

$$E = \frac{1}{z} \sum_{i=1}^{n} V(i)$$ \quad (2.5)

where \(V_i\) indicates the potential of \(i\)th atom caused by the interaction with all atoms in the nanocluster. The potential \(V_i\), where \(i = 1, 2, \ldots, n\) are inspected. The \(V_h\) (highest potential) and \(V_l\) (lowest potential) are sorted out. If \(V_h > vV_l\) where \(v\) is a constant initially set at 0.4, \(V_h\) is considered as the potential for atoms farthest away from the centre of mass and the potential for all the other atoms \((n - 1)\) are displaced.
by \( \delta \), which is also a constant initially set as 0.36. Whereas if \( V_h < \nu V_l \), all the atoms are displaced by \( \delta \).

After getting a new sets of potential, the local minimum energy \( E_{new} \) is calculated again with Equation (2.5). If the \( E_{new} \) calculated is smaller than \( E_{old} \), it will directly replace \( E_{old} \) to be the local minimum energy used for the analysis part. The results are then tested if it falls within a certain confidence level, \( \beta \), where \( 0 < \beta < 1 \). The suitability of parameters \( \delta \) and \( \nu \) are tested until an optimum value of \( \delta \) and \( \nu \) are obtained. The process is repeated until it reached the pre-set maximum steps.

However, there are times where the simulation is unable to satisfy even the lowest confidence level due to the huge energy difference. To overcome this issue, genetic algorithm is introduced to the system in order to rearrange the system configuration.
Start

Generate initial coordinates

Define constants ($\delta$, $\nu$, $\beta$)

Find the local minimal energy for the initial coordinates, $E_{old}$

Sort out highest energy ($V_h$) and lowest energy ($V_l$) for every atom

Check if $V_h > \nu V_l$

Shift atom with $V_h$ to the position furthest away from the origin

Displace all atoms by $\delta$

Displace $(n - 1)$ atoms by $\delta$

Calculate the local minimum energy for new coordinates, $E_{new}$

Check if $E_{new} < E_{old}$

Check if the difference between $E_{old}$ and $E_{new}$ is insignificantly small

Remove $E_{new}$ and remain $E_{old}$

Check if it meets the pre-set maximum steps

Check if results fall within confidence level $\beta$

Amend $\delta$, $\nu$

Stop

Figure 2.3: Flow chart of basin hopping in PTMBHGA.
2.1.4 Multicanonical Basin Hopping

For system involving large number of atoms, the chances of the basin hopping search to fall into a deep potential well in PES is high. Multicanonical basin hopping is introduced to overcome this issue. It is modified from the Boltzmannian Monte Carlo scheme. In terms of multidimensional staircase topography $\tilde{E}(X)$, the non-Boltzmann multicanonical weight factor can be written as:

$$w_{mu}(\tilde{E}) = e^{-\beta^{mu}(\tilde{E})\tilde{E} - \alpha^{mu}(\tilde{E})}$$

(2.6)

where $\beta^{mu}(\tilde{E})$ is an effective inverse temperature while $\alpha^{mu}(\tilde{E})$ is a multicanonical parameter (Hsu et al. 2006).

By applying the weigh factor into basin hopping simulation will help to flatten out the PES and raise the probability for the global minimum search to obtain structure with lower potential energy. The application of multicanonical basin hopping enable the lowest potential energy search to cover wider area in potential energy surface and thus increase the credibility of local potential minimum search.

2.1.5 PTMBHGA Working Parameters

In the PTMBHGA code developed by Hsu (Lai et al. 2002), the empirical Gupta many-body potential is used as the energy calculator. The calculation process involves 3 cycles of basin hopping and multicanonical basin hopping:

First cycle: BH for 100 steps and MBH for 10 steps

Second cycle: BH for 100 steps and MBH for 20 steps

Third cycle: BH for 100 steps and MBH for 30 steps
For the genetic algorithm simulations, PTMBHGA only preserve 75% of the parents’ individuals and replace the remaining 25% with children individuals. The genetic operators used have been weighed as below:

Inversion: 5

Arithmetic mean: 1

Geometric mean: 1

N-point crossover: 5

2-point crossover: 5

The process is repeated with the formation of 20 parents’ individuals (5 newly regenerated) to calculate the lowest potential energy. The simulations ended after 500 steps of GA, which is deemed sufficient for the simulation to obtain the global minimum energy.
2.2 Thermal Properties of Nanoclusters

Thermal properties of nanoclusters have been studied and observed since early of 20th century when Pawlaw explained the reduction in melting temperature of finite system. Thermal properties of a cluster can be studied through melting
process that involves the change in physical state of a matter as temperature varies. Exotic thermal properties found in certain clusters can find applications in e.g., biomedical field where the drugs can be encapsulated into substance made of small particles that melts just above human body temperature (Westesen 2000). Experimental studies on the melting of nanoclusters have been carried out at the end of 20th century by Schmidt et al. using sodium nanocluster (Kusche et al. 1999). In their studies, the nanocluster was heated and the results were compared with sodium in bulk form. The results proved that the melting temperature for nanocluster is lower than in bulk form (Schmidt et al. 1997). Besides, it was proven that the melting transitions of nanocluster does not happen at a finite temperature but spreading out to a finite temperature range. Meanwhile, in the theoretical front, molecular dynamics studies have suggested that melting in nanoclusters could display some unusual behaviour, e.g., emergence of pre-peaks in the melting curves and an extended temperature range throughout which melting is happening.

2.2.1 Brownian Type Isothermal Molecular Dynamics Simulations

In this section, the theoretical basis of Brownian type isothermal MD, will be discussed. Implementation of this MD approach in the form of a software package has been developed by S. K. Lai’s team in National Central University, Taiwan. The team developed the code in year 2007 - based on the ideas inspired by Nose, Hoover and Kusnezov (Bulgac et al. 1990). The Brownian Type Isothermal Molecular Dynamics code (abbreviated BTIMD) used in this thesis is provided by the NCU group with kind courtesy.
The basic idea of this MD simulation approach is built upon canonical ensemble at classical level, and is designed with the intention to study melting behaviour of clusters (Yen et al. 2007). As in most MD approach to model thermodynamically related simulations, such as melting phenomena, temperature of the system has to be stipulated in a controlled manner. To this end, heat bath is coupled to the system to heat it up to a desired temperature. The temperature-tuning control in the MD simulation will require additional degree of freedom. In the case of BTIMD, the additional degree of freedom come in the form of pseudofriction terms that couple the heat bath to the simulated system via a cubic coupling scheme (CCS) which provides superiority over other MD approaches. The application of CCS managed to overcome the downsides of Nose-Hoover method, which are the dependency on (1) the assumption that the motion is ergodic, (2) the reliance of initial conditions, (3) algorithm parameters and, (4) pseudofriction terms (Kusnezov et al. 1990). The phase space of the system can be explored at fast exploration rate and ergodicity can be ensured (reproduced the canonical ensemble averages) with the involvement of CCS. The modified CCS involved three pseudofriction terms, which are sufficient to produce ergodic condition for free particles in contact with a thermal bath. The technical details of the CCS is compactly summarised in the equation below:

\[
\dot{x}_{i(a)} = \frac{p_{i(a)x}}{m_a} \quad (2.7)
\]

\[
\dot{p}_{i(a, x)} = -\frac{\partial E_n}{\partial x_{i(a)}} - \frac{\alpha_{a, x}^e 0, a}{n L_a} \mu_{a, x}^3 \frac{p_{i(a), x}}{p_{0, a}^x} - \beta_{a, x}^e 0, a \nu_{a, x} \left( \frac{p_{i(a), x}^2}{p_{0, a}^x} - d_0 \right) - \frac{x_{a, x}^e 0, a}{n L_a} \eta_{a, x} \frac{p_{i(a), x}^3}{p_{0, a}^x} \quad (2.8)
\]

\[
\mu_{a, x} = \frac{\alpha_{a, x} T}{p_{0, a} L_a} \left( \sum_{i=1}^n \frac{p_{i(a), x}^2}{nm_a T} + \sum_{i=1}^n \frac{p_{i(b), x}^2}{nm_b T} - 1 \right) \quad (2.9)
\]
\[ \dot{v}_{a,x} = \frac{p_{0,a}}{p_{0,a}^0} \left( \frac{n_{i=1}^a P_{i(a),x}^3}{nm_a T_{p_0,a}} + \frac{n_{i=1}^b P_{i(b),x}^3}{nm_b T_{p_0,b}} - d_0 \frac{\sum_{i=1}^a P_{i(a),x} P_{0,a}}{nm_a} \right) \]

\[ \dot{\eta}_{a,x} = \frac{x_{a,r}}{p_{0,a}^0} \left( \frac{\sum_{i=1}^a P_{i(a),x}^4}{nm_a T_{p_0,a}} + \frac{\sum_{i=1}^b P_{i(b),x}^4}{nm_b T_{p_0,b}} - 2 \frac{\sum_{i=1}^a P_{i(a),x}^2}{nP_{0,a}} - \frac{3 \sum_{i=1}^b P_{i(b),x}^2}{nP_{0,b}} \right) \]

In the equations 2.7 to 2.11, \( x_{i(a)} \) and \( x_{i(b)} \) are the x-component position coordinate, \( P_{i(a),x} \) and \( P_{i(b),x} \) are the x-component momentum, \( E_n \) is the potential energy defined from the Gupta many-body potential, \( \mu_{a,x}, v_{a,x} \), and \( \eta_{a,x} \) are the x-component pseudofriction coefficient, \( m_a \) is the atomic mass, \( p_{0,a} = \sqrt{2m_a T} \) is the average thermal momentum at temperature \( T \), \( d_0 \) is the dimensionless constant, \( L_0 \) is a constant with dimension of length, \( e_{0,a} \) is the energy constant with value estimated from \( e_{0,a} \sim m_a L_0^2 \omega_D^2 / (4\pi^2) \), while \( \omega_D \) is the Debye frequency, \( \alpha_a \sim \beta_a \sim \kappa_a \sim \sqrt{\left[ m_a L_0^2 \right]^{1/2}} \), in which \( t_0 = 2\pi / \omega_D \).

2.2.2 Procedures of Molecular Dynamics Simulations

All the MD simulations in this thesis were conducted using the BTIMD code provided by the NCU group. Throughout all simulations, time step of \( \Delta t \) which is fixed between \( 1 \times 10^{-15} \) to \( 5 \times 10^{-15} \) s was used. For lower temperature (\( T \leq 500 \) K), the simulation runs were carried out for a total of \( 1 \times 10^8 \) steps so that the effect of large fluctuations during the melting can be circumvented by sampling a large amount of data via a lengthy simulation. Meanwhile, for gold-platinum nanocluster at higher temperatures (\( 550 \) K \( \leq T \leq 1050 \) K), \( 2 \times 10^8 \) steps were performed to produce smoothened resulting graphs and improve the reliability of the
simulation results. At the end of $2 \times 10^8$ steps run for case of temperature, $T \geq 1100$ K, an additional $2 \times 10^7$ steps were carried out. The total elapsed time $t_{tot}$ for a complete simulation was always fixed at $1 \times 10^{-7}$ s.

The MD simulations were run at an interval of 50 K throughout all temperatures. However, in pre-melting and melting regions, which generally lies in the range of $700$ K $\leq T \leq 1050$ K, a more refined interval of 10 K is adopted.

2.3 Ultrafast Shape Recognition

Molecular shape recognition technique is widely applied in chemistry field to categorize molecular structures, especially proteins structure. It has been experimentally proven to be an important tool to discover new materials (Boström et al. 2006). There are currently 2 types of shape recognition algorithm, namely, superposition-based shape comparison and superposition free algorithm (Ebalunode et al. 2010). The superposition-based shape similarity comparison algorithm was introduced in 1991 (Meyer et al. 1991). The downside of this algorithm is the time-consuming optimization process. To overcome this weak point, superposition-free algorithm that is based on the interatomic distance has been invented. This technique was named as Ultrafast Shape Recognition (USR) in a paper published in 2007 by Ballester et al. The technique has successfully speeded up the process of fast virtual screening (Ballester et al. 2009). The idea of USR ideology was inspired S. K. Lai’s team from National Central University, Taiwan to come up with a novel approach for analysing metallic clusters undergoing thermodynamic transition.

The analysing process of USR involved the shape similarity index and probability of shape similarity function. It compares the reference ground-state
configuration of the original nanocluster at 0 K against the configuration at each time step during the simulation. The shape similarity index $\zeta$ is the quantifier used to measure the difference between the structures of the nanoclusters $i = 0$. Referring to Ballester et al., shape similarity index is defined as

$$\zeta_i = \left[1 + \sum_{j=1}^{m} |M_{i,j} - M_{0,j}|/m\right]^{-1}$$  \hspace{1cm} (2.12)

where $i$ refers to the $i$th structural arrangement of the system at a given instance in a MD simulation, $m$ is the total number of statistical moment descriptors to be included in the definition of $\zeta$. The reference structure has the value $\zeta_i = 1$ when $i = 0$. Therefore, the value of $\zeta_i$ is less than 1 for any $i$th structure arrangements that is different from the reference structure. $\{M_{0,1}, M_{0,2}, \ldots, M_{0,m}\}$ refer to the moments of atomic distance distribution of the reference structure, while $\{M_{i,1}, M_{i,2}, \ldots, M_{i,m}\}$ refer to that of the $i$th arrangement.

Given the collection of a cluster’s statistical data generated in a MD simulation, 4 different statistical moments, which are defined based on the 3D spatial coordinates of the atoms, can be defined, namely,

(i) Mean value
(ii) Variance
(iii) Skewness
(iv) Kurtosis
These moments in turns can be calculated by referring to 4 different reference sites (origins), namely,

(i) Centre of mass (COM)

(ii) Atom closest to the centre of mass (CCM)

(iii) Atom farthest from the centre of mass (FCM)

(iv) Atom farthest to atom farthest from the centre of mass (FTF)

Hence, overall, 16 different statistical moment descriptors can be discerned (only 12 moments are formally identified in Ballester et al. 2007). In other words, \( m = 16 \) as appear in the summation in Equation (2.12).

The definitions of 4 reference sites are given below, along with illustrating examples to facilitate the explanation.

(i) **Centre of mass (COM)**

![Figure 2.5: The location of COM in Au\(_{32}\)Pt\(_6\) ground-state structure. (Olive green represents platinum atoms and pink represents gold atoms)](image)

Centre of mass refers to the mean position of all the individual atoms in the nanocluster. Generally, COM of a given cluster may not coincide with any particular atom sitting inside the cluster. Rather, it may fall on a spatial point located in an
intermediate location between the atoms. Using Au$_{32}$Pt$_6$ ground-state structure as an illustration, its COM is a point located between two Au atoms sitting in the middle-most of the cluster.

(ii) **Atom closest to the centre of mass (CCM)**

![Figure 2.6: The location of CCM atom in Au$_{32}$Pt$_6$ ground-state structure.](image)

Generally, CCM refers to the atom which is nearest to the COM. Specifically in Au$_{32}$Pt$_6$, CCM may refer to either one of the two Au atoms which is closest to the COM, such as illustrated in Figure 2.6.

(iii) **Atoms farthest from the centre of mass (FCM)**

![Figure 2.7: The location of FCM atom in Au$_{32}$Pt$_6$ ground-state structure.](image)
FCM refers to the atom which is farthest away from the COM. However, it may refer to more than one unique atom if the nanocluster is symmetrical enough to have several equidistant FCMs. In the special case of \( \text{Au}_{32}\text{Pt}_6 \), FCM is illustrated in Figure 2.7.

(iv) **Atom farthest to FCM (FTF)**

![Figure 2.8: The location of FCM atom in \( \text{Au}_{32}\text{Pt}_6 \) ground-state structure.](image)

FTF refers to the atom which is farthest away from the FCM. Unlike CCM and FCM, FTF does not refer to COM for directly. Instead, it takes FCM as a reference point, resulting in an indirect relationship between COM and FTF. In the special case of \( \text{Au}_{32}\text{Pt}_6 \), FTF is illustrated in Figure 2.8.
CHAPTER 3

GROUND-STATE STRUCTURES

Following the procedures as outlines in Chapter 2, initial random configurations of Au and Pt nanoclusters are used as initial input into the PTMBHGA global minimum search algorithm to produce lowest-energy configurations of Au-Pt nanoclusters, ranging from pure Au to Pt clusters, and various mixed compositions in the between. These ground-state structures will be systematically presented and discussed in this Chapter. They are then subjected to a heating procedure using BTIMD. Analysis of the melting dynamics based on the time evolution of ultrafast shape recognition is also performed and reported.

3.1 Ground-State Structure for Nanoclusters

Magic nanoclusters are nanoclusters the display strong stability at certain sizes (number of atoms). It has been observed that for pure nanoclusters, 7, 13, 19, 25, 33, 38 and 55 are examples of magic number with high stability (Baletto et al. 2004). Therefore, in this thesis, before zooming into the bi-metallic clusters, calculations are first conducted for pure gold and pure platinum clusters for sizes ranging from 3 to 55, which covers these magic numbers. These calculations also serve the purpose of verifying whether the PTMBHGA code with Gupta potential reproduces the same ground-state structures as already published in the literature.
At this point, it is remarked here that for bimetallic clusters, magic numbers occur at 34, 38, 55. Bimetallic nanoclusters form core-shell structures at these magic numbers.

3.1.1 **Ground-State Structures of Pure Gold Nanoclusters**

This section presents the calculated results for pure gold nanoclusters produced by PTMBHGA for the size of \( n = 3 \) up to \( n = 55 \). The results of gold nanoclusters (3 - 38 atoms) obtained from the calculations are compared with that published data in a reference paper (Xia Wu et al. 2012). The geometries of the gold nanoclusters are shown in Figure 3.1.
Figure 3.1: The comparison between the structures of gold nanoclusters obtained from PTMBHGA (upper) and reference (below) from Xia Wu et al. 2012.

From the results shown in Figure 3.1, several ground-state structures obtained from the PTMBHGA are similar to that published in the work by Xia Wu et al. 2012. For gold nanoclusters $n \leq 20$, most of the structures appeared to be similar except that for $n = 9$, 14 and 17. On the other hand, the lowest-energy structures for $21 \leq n \leq 38$ differ slightly from the reference. However, it is not possible to compare the
energies between this two sets of structures because the reference has not reported their energies. Table 3.1 shows the minimum potential energy obtained from PTMBHGA simulations.

Table 3.1: The minimum potential energy for gold nanoclusters obtained from PTMBHGA.

<table>
<thead>
<tr>
<th>n (Au)</th>
<th>$E_n$ (eV)</th>
<th>n (Au)</th>
<th>$E_n$ (eV)</th>
<th>n (Au)</th>
<th>$E_n$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-7.21</td>
<td>21</td>
<td>-67.92</td>
<td>39</td>
<td>-131.18</td>
</tr>
<tr>
<td>4</td>
<td>-10.65</td>
<td>22</td>
<td>-71.53</td>
<td>40</td>
<td>-134.60</td>
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<tr>
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<td>-13.91</td>
<td>23</td>
<td>-75.03</td>
<td>41</td>
<td>-138.13</td>
</tr>
<tr>
<td>6</td>
<td>-17.30</td>
<td>24</td>
<td>-78.41</td>
<td>42</td>
<td>-141.57</td>
</tr>
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<td>8</td>
<td>-23.79</td>
<td>26</td>
<td>-85.40</td>
<td>44</td>
<td>-148.65</td>
</tr>
<tr>
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<td>-27.22</td>
<td>27</td>
<td>-88.83</td>
<td>45</td>
<td>-152.24</td>
</tr>
<tr>
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<td>-30.56</td>
<td>28</td>
<td>-92.31</td>
<td>46</td>
<td>-155.64</td>
</tr>
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<td>-159.22</td>
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<td>-37.24</td>
<td>30</td>
<td>-99.30</td>
<td>48</td>
<td>-163.01</td>
</tr>
<tr>
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<td>-41.04</td>
<td>31</td>
<td>-102.82</td>
<td>49</td>
<td>-166.43</td>
</tr>
<tr>
<td>14</td>
<td>-44.13</td>
<td>32</td>
<td>-106.27</td>
<td>50</td>
<td>-170.04</td>
</tr>
<tr>
<td>15</td>
<td>-47.58</td>
<td>33</td>
<td>-109.92</td>
<td>51</td>
<td>-173.53</td>
</tr>
<tr>
<td>16</td>
<td>-50.96</td>
<td>34</td>
<td>-113.35</td>
<td>52</td>
<td>-177.18</td>
</tr>
<tr>
<td>17</td>
<td>-54.37</td>
<td>35</td>
<td>-116.93</td>
<td>53</td>
<td>-180.75</td>
</tr>
<tr>
<td>18</td>
<td>-57.76</td>
<td>36</td>
<td>-120.39</td>
<td>54</td>
<td>-184.54</td>
</tr>
<tr>
<td>19</td>
<td>-61.12</td>
<td>37</td>
<td>-124.06</td>
<td>55</td>
<td>-187.96</td>
</tr>
<tr>
<td>20</td>
<td>-64.55</td>
<td>38</td>
<td>-127.76</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Second energy difference, which is an indicator to monitor the relative stability of nanoclusters, based on the definition in Eq. (3.1), are calculated from the data in Table 3.1.

$$\Delta_2E = E_{n+1} + E_{n-1} - (2E_n)$$  \hspace{1cm} (3.1)
The plot of the second energy difference is shown in Figure 3.2 to ease the process of data analysis. A large value at a particular cluster size in second energy difference plot implies higher relative stability compared to neighbouring cluster sizes.

Figure 3.2: The second energy difference plot for gold nanoclusters from size 3-55 atoms.

Comparing Figure 3.2 against the geometry of the structures obtained with PTMBHGA in Figure 3.1, it is found that nanoclusters with higher symmetry tends to have higher relative stability. The symmetry for every cluster has been obtained by using the VMD software package with a tolerance of 0.05. Gold nanoclusters with high relative stability are identified and summarised in Table 3.2, along with the corresponding symmetry groups.
Table 3.2: Structures of gold nanoclusters with high symmetry and relative stability.

<table>
<thead>
<tr>
<th>$n$ (Au)</th>
<th>Symmetry</th>
<th>Symmetry order</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>T$_d$</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>D$_{5h}$</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>I$_h$</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>C$_{2v}$</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>C$_s$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>O$_h$</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>$n$ (Au)</td>
<td>Symmetry</td>
<td>Symmetry order</td>
<td>Structure</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>----------------</td>
<td>-----------</td>
</tr>
<tr>
<td>43</td>
<td>$C_{2v}$</td>
<td>4</td>
<td>![Image]</td>
</tr>
<tr>
<td>45</td>
<td>$C_{2v}$</td>
<td>4</td>
<td>![Image]</td>
</tr>
<tr>
<td>48</td>
<td>$C_{2v}$</td>
<td>4</td>
<td>![Image]</td>
</tr>
<tr>
<td>54</td>
<td>$I_h$</td>
<td>120</td>
<td>![Image]</td>
</tr>
<tr>
<td>55</td>
<td>$I_h$</td>
<td>120</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

From Table 3.2, there are three occurrences (namely sizes 13, 54 and 55) of highly stable structures with the highest possible order of 120 (which corresponds to icosahedron $I_h$). Despite a common highest symmetry group $I_h$, the second energy difference against the number of gold nanoclusters plot shows a difference in relative stability. This is due to the definition of relative stability from Eq. 3.1 with respect to
the neighbouring atoms \((n + 1)\) and \((n – 1)\). (Lin et al. 2013). Therefore, the relative stability for 55 atoms of gold nanocluster is almost nil as it has the same stability with 54 atoms of gold nanoclusters.

3.1.2 Ground-State Structures of Pure Platinum Nanoclusters

In this section the results produced from PTMBHGA for pure platinum nanoclusters from sizes 3 to 55 atoms are presented. The energies for these clusters are tabled in Table 3.3. Compared to Table 3.1, the minimized potential energy of a platinum nanocluster is much lower than that of a corresponding gold cluster with the same size.

Table 3.3: The minimum potential energy for platinum nanoclusters obtained from PTMBHGA.

<table>
<thead>
<tr>
<th>(n) (Pt)</th>
<th>(E_n) (eV)</th>
<th>(n) (Pt)</th>
<th>(E_n) (eV)</th>
<th>(n) (Pt)</th>
<th>(E_n) (eV)</th>
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</thead>
<tbody>
<tr>
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<td>-213.26</td>
</tr>
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<td>4</td>
<td>-18.22</td>
<td>22</td>
<td>-117.24</td>
<td>40</td>
<td>-218.85</td>
</tr>
<tr>
<td>5</td>
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<td>-122.86</td>
<td>41</td>
<td>-224.49</td>
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</tr>
<tr>
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<td>-34.54</td>
<td>25</td>
<td>-133.92</td>
<td>43</td>
<td>-235.94</td>
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<td>26</td>
<td>-139.53</td>
<td>44</td>
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<td>45</td>
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<td>-150.88</td>
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<td>-252.91</td>
</tr>
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<td>-156.57</td>
<td>47</td>
<td>-258.67</td>
</tr>
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<td>12</td>
<td>-61.45</td>
<td>30</td>
<td>-162.31</td>
<td>48</td>
<td>-264.41</td>
</tr>
<tr>
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<td>-67.43</td>
<td>31</td>
<td>-167.65</td>
<td>49</td>
<td>-269.99</td>
</tr>
<tr>
<td>14</td>
<td>-72.60</td>
<td>32</td>
<td>-173.37</td>
<td>50</td>
<td>-275.86</td>
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<tr>
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<td>-179.07</td>
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<td>-281.45</td>
</tr>
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<td>-83.94</td>
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<td>-184.76</td>
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<td>-287.25</td>
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<td>-190.34</td>
<td>53</td>
<td>-292.93</td>
</tr>
<tr>
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<td>-95.00</td>
<td>36</td>
<td>-195.99</td>
<td>54</td>
<td>-298.84</td>
</tr>
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<td>-100.45</td>
<td>37</td>
<td>-201.85</td>
<td>55</td>
<td>-304.28</td>
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<tr>
<td>20</td>
<td>-105.92</td>
<td>38</td>
<td>-207.68</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.3: The second energy difference plot for platinum nanoclusters from size 3-55 atoms.

The second energy difference graph of platinum nanoclusters differs slightly from gold nanoclusters as the structures of pure platinum nanoclusters and gold nanoclusters with the same number of atoms are different. Pure platinum nanoclusters with higher relative stability are summarised in Table 3.4. Icosahedral structure is predicted to be the structure with highest relative stability.
Table 3.4: Structures of high symmetry and relative stability platinum nanoclusters.

<table>
<thead>
<tr>
<th>$n$ (Pt)</th>
<th>Symmetry</th>
<th>Symmetry order</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$T_d$</td>
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<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td>13</td>
<td>$I_h$</td>
<td>120</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>30</td>
<td>$C_{3v}$</td>
<td>6</td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>38</td>
<td>$O_h$</td>
<td>48</td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>43</td>
<td>$C_{2v}$</td>
<td>4</td>
<td><img src="image5" alt="Image" /></td>
</tr>
<tr>
<td>48</td>
<td>$C_{2v}$</td>
<td>4</td>
<td><img src="image6" alt="Image" /></td>
</tr>
</tbody>
</table>
3.1.3 Ground-State Structures of Gold-platinum Nanoclusters

The results generated by PTMBHGA in the previous sections for pure-clusters have shown to provide a reliable starting point to advance into bimetallic case. To this end, only Au-Pt clusters with a fixed size of 38 atoms but variable composition will be considered. i.e. \( \text{Au}_n \text{Pt}_{38-n} \), where \( 0 \leq n \leq 38 \). In the bimetallic case, the variable \( n \) refers to the number of gold atom in the \( \text{Au}_n \text{Pt}_{38-n} \) clusters.

The reason for choosing 38 atoms, as mentioned earlier, is because cluster of this size has a high possibility of displaying core-shell segregation. The results of the optimized potential energy for every composition obtained from the present PTMBHGA calculation are tabled in Table 3.5. The plot of second energy difference
shows that the 38-atom binary cluster with a composition of 32 gold + 6 platinum atoms is the most stable one.

Table 3.5: The minimum potential energy for gold-platinum nanoclusters obtained from PTMBHGA.

<table>
<thead>
<tr>
<th>$E_n$ (eV)</th>
<th>$E_n$ (eV)</th>
<th>$E_n$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{38}$</td>
<td>-207.68</td>
<td>Au$<em>{13}$Pt$</em>{25}$ -182.89</td>
</tr>
<tr>
<td>Au$<em>1$Pt$</em>{37}$</td>
<td>-205.71</td>
<td>Au$<em>{14}$Pt$</em>{24}$ -180.91</td>
</tr>
<tr>
<td>Au$<em>2$Pt$</em>{36}$</td>
<td>-203.81</td>
<td>Au$<em>{15}$Pt$</em>{23}$ -179.11</td>
</tr>
<tr>
<td>Au$<em>3$Pt$</em>{35}$</td>
<td>-201.92</td>
<td>Au$<em>{16}$Pt$</em>{22}$ -177.21</td>
</tr>
<tr>
<td>Au$<em>4$Pt$</em>{34}$</td>
<td>-200.03</td>
<td>Au$<em>{17}$Pt$</em>{21}$ -175.24</td>
</tr>
<tr>
<td>Au$<em>5$Pt$</em>{33}$</td>
<td>-198.18</td>
<td>Au$<em>{18}$Pt$</em>{20}$ -173.34</td>
</tr>
<tr>
<td>Au$<em>6$Pt$</em>{32}$</td>
<td>-196.29</td>
<td>Au$<em>{19}$Pt$</em>{19}$ -171.47</td>
</tr>
<tr>
<td>Au$<em>7$Pt$</em>{31}$</td>
<td>-194.44</td>
<td>Au$<em>{20}$Pt$</em>{18}$ -169.56</td>
</tr>
<tr>
<td>Au$<em>8$Pt$</em>{30}$</td>
<td>-192.51</td>
<td>Au$<em>{21}$Pt$</em>{17}$ -167.86</td>
</tr>
<tr>
<td>Au$<em>9$Pt$</em>{29}$</td>
<td>-190.63</td>
<td>Au$<em>{22}$Pt$</em>{16}$ -165.96</td>
</tr>
<tr>
<td>Au$<em>{10}$Pt$</em>{28}$</td>
<td>-188.68</td>
<td>Au$<em>{23}$Pt$</em>{15}$ -164.08</td>
</tr>
<tr>
<td>Au$<em>{11}$Pt$</em>{27}$</td>
<td>-186.79</td>
<td>Au$<em>{24}$Pt$</em>{14}$ -162.13</td>
</tr>
<tr>
<td>Au$<em>{12}$Pt$</em>{26}$</td>
<td>-184.84</td>
<td>Au$<em>{25}$Pt$</em>{13}$ -160.28</td>
</tr>
</tbody>
</table>

Table 3.5 shows that the increase in gold composition in the gold-platinum nanoclusters leads to the increase in the optimized potential $E_n$ (eV).
Figure 3.4: The second energy difference plot for gold-platinum nanoclusters of 38 atoms for every composition. $n$ refers to the number of gold atom in the bimetallic clusters $\text{Au}_n\text{Pt}_{38-n}$.

Visual inspection alone is sufficient to spot that a core-shell segregation trend among the composite atoms is occurring in these optimized binary clusters as the gold composition number $n$ increase. Specifically, the core of these core-shell structures is occupied by platinum atoms while the shell by gold atoms.

As $n$ increases, the optimized binary clusters display a trend in which gold atoms tend to occupy the core position while platinum atoms reside on the outer shell. The trend begins with a truncated octahedron when the number of gold atoms $n$ increases from $n = 1$ onwards. According to Bochicchio et al. 2013, the core shell segregation observed in the Au-Pt clusters might be due to the smaller surface energy of gold atom as compared to the platinum atom.

Four highly stable gold-platinum nanoclusters obtained from the PTMBHGA + Gupta potential calculations are identified, namely that with gold composition $n =$
15, 25, 30 and 32. These clusters will be selected for further analysis. It is observed that the core of \( \text{Au}_{25}\text{Pt}_{13} \) cluster is an icosahedral of platinum atoms, while the Au that in the \( \text{Au}_{32}\text{Pt}_6 \), the most stable bimetallic cluster studied in this thesis, is a hexagonal ring. The \( \text{Au}_{32}\text{Pt}_6 \) cluster is specifically selected for further investigation for its thermal properties.

Table 3.6: Structures of gold-platinum nanoclusters with high symmetry and relative stability. The army green spheres in the core of these clusters represent platinum atoms while that in the shell gold atoms.

<table>
<thead>
<tr>
<th>( n ) (Pt)</th>
<th>Symmetry</th>
<th>Symmetry order</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image" alt="Structure 15" /></td>
</tr>
<tr>
<td>25</td>
<td>( I_h )</td>
<td>120</td>
<td><img src="image" alt="Structure 25" /></td>
</tr>
<tr>
<td>30</td>
<td>( C_{3v} )</td>
<td>6</td>
<td><img src="image" alt="Structure 30" /></td>
</tr>
<tr>
<td>32</td>
<td>( D_{6h} )</td>
<td>24</td>
<td><img src="image" alt="Structure 32" /></td>
</tr>
</tbody>
</table>
CHAPTER 4

MELTING BEHAVIOUR OF NANOCLUSTERS

One of the main purposes of this thesis is to investigate the detailed mechanism of the melting phenomena in the Au-Pt nanoclusters. This can be done thermally annealing the ground-state structures reported in the previous Chapters. Numerical data generated using Brownian type isothermal molecular dynamics simulations are then post-processed so that the melting behaviour can be analysed and quantified. The evolution of certain thermally-relevant descriptors is usually monitored for the purpose of investigating the phenomena of cluster melting, including specific heat, Lindemann index, velocity autocorrelation function, power spectrum, etc. In this thesis, the melting mechanism of Au-Pt clusters is to be analysed in terms of two specific descriptors, namely specific heat and Lindemann index.

The numerical results will be presented and discussed in the following.

4.1 Specific Heat

The first indicator used to quantify the melting properties of the binary alloy clusters is specific heat, $C_v$, which is one of the most commonly indicators used in the literature. Numerically, $C_v$ in a MD simulation can be evaluated via

$$C_v(T) = \frac{\langle (E_{total})^2 \rangle - \langle E_{total} \rangle^2}{k_BT^2}$$

(4.1)
where \( E_{\text{total}} = (\sum_{i(a)} p^2_{i(a)}/(2m_a) + \sum_{i(b)} p^2_{i(b)}/(2m_b)) + E_n \). Based on the definition Eq. (4.1) one can interpret specific heat as a measure in the fluctuations of energy.

### 4.2 Lindemann Index

The second indicator used in this thesis to quantify the melting behaviour of the clusters is Lindemann index, which is also a common tool used to study variation in geometrical properties of a nanocluster in a thermal process. Lindemnn index, \( \delta \), is given as the relative root-mean-square (rms) of bond length fluctuations as per:

\[
\delta = \frac{1}{n(n-1)} \sum_{i=1}^{n} \sum_{j \neq i} \frac{\sqrt{(r_{ij}(t))^2 - (\langle r_{ij}(t) \rangle)^2}}{(\langle r_{ij}(t) \rangle)}
\]

where \( n \) denotes the number of atoms in the nanocluster and \( r_{ij} \) refers to the relative bond length at temperature \( t \). In this thesis, \( \delta \) at different temperatures will be sampled from the MD simulations. Data of these \( \delta \) will be post-processed so that its temperature-dependent pattern can be analysed.

At low temperatures, \( \delta \) remains small. This is justifiable as the rms bond length fluctuations of the clusters is expected to be small, and nearly constant (Hsu et al. 2008).

On the other hand, higher \( \delta \) values are expected at higher temperatures as atoms within the nanocluster vibrates more vigorously as temperature rises. High \( \delta \) value also suggest that the bond length fluctuates more within the nanocluster. When the value of \( \delta \) exceeds certain prescribed threshold, it implies that the nanocluster has undergone some structural change. A structural change induced by increasing
temperature is usually associated with the occurrence of a melting process. The bond length of a nanocluster is relatively smaller than that during or after the melting process. Furthermore, the atoms within the nanocluster vibrate more vigorously as temperature rises.

4.3 Test Case: \textbf{Au}_{12}\textbf{Cu}_{1}

As a test case to measure the melting process in the BTIMD code, a melting simulation for 13-atoms of gold-copper nanocluster, \textit{Au}_{12}\textit{Cu}_{1}, was carried out. The melting of \textit{Au}_{12}\textit{Cu}_{1} cluster has been reported by Yen \textit{et al} in 2009 (Yen \textit{et al.} 2009) using the same code and procedure. The present test simulation is performed with the purpose to verify the correctness of the simulation technique by referring to Yen \textit{et al.} 2009 as a benchmark.

The ground-state structure for \textit{Au}_{12}\textit{Cu}_{1} is required as an input ingredient for running the melting simulation with the BTIMD code. According to the published work by Yen \textit{et al}, 2009, the ground-state structure also obtained with the same PTMBHGA code. In the present case, the PTMBHGA code was used to generate the \textit{Au}_{12}\textit{Cu}_{1} ground-state structure, which is then fed into the BTIMD code as initial configuration for running melting simulations. Indeed, not only for the present case of \textit{Au}_{12}\textit{Cu}_{1}, all ground-state structures reported in this thesis were obtained using the same PTMBHGA code (along with this built-in Gupta potentials) originally used by Yen \textit{et al}. The code was made available to us thanks to the courtesy of the NCU group who developed it.
The numerical results of the heat capacity and Lindemann index of the $\text{Au}_{12}\text{Cu}_1$ cluster, obtained by post-processing the MD data, are shown in Figure 4.1 as functions of temperature.

![Graph of specific heat $C_v$ (continuous line) and Lindemann Index $\delta$ (dotted line) against temperature for $\text{Au}_{12}\text{Cu}_1$ nanocluster.](image)

**Figure 4.1:** Graph of specific heat $C_v$ (continuous line) and Lindemann Index $\delta$ (dotted line) against temperature for $\text{Au}_{12}\text{Cu}_1$ nanocluster.

The graphs in Figure 4.1 show the trend of specific heat $C_v$ and Lindemann index $\delta$ against temperature (in Kelvin). $C_v$ is represented by the dotted curve, while $\delta$ the continuous curve. The $C_v$ curve, which increases at a rather slow pace below $T \approx 700$ K, picks up a rapidly increasing rate and climbs quite sharply to reach to the peak value at $\approx 1000$ K, the temperature at which melting of the cluster occurs. For the $\delta$ curve, it is rather flat below 550 K, after which it rises quite abruptly. In contrast, the $C_v$ curve does not display obvious threshold behaviour when it crosses this temperature. A drastic rise in the $C_v$ curve is delayed until the temperature reaches $\approx 700$ K. Besides, the variation in $\delta$ in the range of temperature from $\approx 700$ K to $\approx 1100$ K is relatively mild, in contrast to $C_v$ which varies sharply when temperature crosses the $C_v$ peak at $\approx 1100$ K. The relatively high melting temperature
of 1100 K is due to the high stability of structure of the 13-atom gold-copper nanocluster, which is in icosahedron with its only Cu atom located at the centre.

As the temperature reaches 1100 K, the surface atoms (Au) were visually observed to start permuting but the overall icosahedral topology of the cluster remained. This phenomenon is known as surface melting. As mentioned in section 4.1 and 4.2, \( C_v \) is the measure of energetic changes and \( \delta \) is the measure of structural change. The quantitative difference in the nature of these two descriptors is reflected in the difference of the behavioural trend displayed by the two curves. Each of these descriptors capture statistical information of a different quantitative nature which may not be sensitively picked up by the other. In the present surface melting, \( \delta \) did not sensitively pick up the relevant signal (the \( \delta \) curve at 1100 K does not display obviously recognizable variations), while the \( C_v \) curves did.

From Figure 4.1, a sharp melting range is identified at around 1100 K, which is the peak displayed by the \( C_v \) curve. This result is quantitatively agrees with that obtained by the original author of the code as reported in Yen et al. 2009, which prove that the code in this thesis is effective. The relevant plots from Yen et al. 2009 are reproduced in Figure 4.2.

![Figure 4.2](a) and (b): (a) specific heat \( C_v \) and (b) Lindemann Index \( \delta \) against temperature for \( \text{Au}_{12}\text{Cu}_1 \) obtained by Yen et al., 2009.
4.4 $\text{Au}_{32}\text{Pt}_6$

Figure 4.3: Graph of specific heat $C_v$ (continuous line) and Lindemann Index $\delta$ (dotted line) against temperature for $\text{Au}_{32}\text{Pt}_6$ nanocluster.

To limit the scope of investigation, this thesis will focus on a particular cluster consist of a relatively large number of atoms, $\text{Au}_{32}\text{Pt}_6$. The $C_v$ and $\delta$ plots against temperature are shown in Figure 4.3. In the low temperature range of less than $\approx 700$ K, both $C_v$ and $\delta$ curves display similar trend of mild and graduate increment with temperature. As it turns out, the melting process involved a pre-melting phase, which caused the appearance of a sudden sharp peak in the graph around 700 K to 800 K (shown as shaded region in Figure 4.3). In this temperature range, the 2-dimensional six hexagonal platinum atoms deformed into a 3-dimensional structure with gold atoms remained at the surface and platinum atoms at core. The dynamical evolution of the cluster was visually observed from the video produced by MD simulation.
The peak of the \( C_v \) curve discloses that melting of this cluster occurred between 1000 K and 1050 K. The geometrical structure of \( \text{Au}_{32}\text{Pt}_6 \) changed completely as the platinum core atoms started to migrate to the surface of the nanocluster and no longer connected to one another. The shape of the whole structure subsequently turn in an random structure at higher temperature. The snapshots of the cluster at selected temperatures are attached in the Appendix.

### 4.5 Post-Processing with Ultrafast Shape Recognition

A large amount of numerical data was obtained from the BTIMD code, containing MD trajectory files of the \( \text{Au}_{32}\text{Pt}_6 \) cluster equilibrated at many fixed temperatures (specifically, 100 K, 150 K, …, 700 K, 710 K, 720 K, …, 1000 K, 1050 K, 1100 K, 1150 K, …, 2000 K). These fixed-temperature trajectory data are post-processed so that the variations in the configuration of the nanocluster at each temperature can be recognized for analysing the melting mechanism. To this end, a code, nicknamed USR, which was originally written by T.W. Yen from the NCU group, was used. Basically, the USR code was used to produce two types of statistical data for analysing the melting mechanism.

The first type of statistical data produced from the USR code (by post-processing the trajectory data from BTIMD code) are COM atomic distance plots. Each COM atomic distance plot is obtained from every 500 time-steps of a huge collection of recorded snapshots of cluster configuration along a simulated MD trajectory, in which the simulation is equilibrated at a fixed temperature \( T \) by using the CCS thermostat implemented in the BTIMD code. The vertical axis in a USR graph represent atomic distances in unit of Angstrom, while the horizontal axis
represents the numerical label attached to a fixed atom in the cluster. For example, for the 38-atom $\text{Au}_{32}\text{Pt}_{6}$ cluster studied in this thesis, the six Pt atoms are labelled as 2, 3, 4, 35, 36 and 37 respectively, whereas the other numbers (i.e., 1, 5, 6, …, 33, 34, 38) label the individual Au atoms. A COM atomic distance plot displays the atomic distance of each atom as measured from the COM reference site of the nanocluster, which is defined in section 2.3 Ultrafast shape recognition. A black line is used to link up all these points in a COM atomic distance plot. Independently, a blue line will be overlaid on top of any COM atomic distance plot. This blue line represents the atom-to-COM distances in a reference structure, which is taken to be the ground state structure at 0 K. As such, the atomic distance plots (the black line) will manifest different profiles at different temperatures, but the blue line (which serves as a reference profile) remains unique. The black line, which is obtained at non-zero temperature $T$, in general does not coincide with the blue line except at low temperatures. The blue reference profile provides a convenient visual aid as how the black line, which measures the atomic distances with respect to the current COM, deviate from that of the reference structure at 0 K.

In a COM atomic distance plot, the points representing the atomic distance of the Pt atoms will be marked with circles to aid visual intuition. The $y$-coordinates of the circles in a COM atomic distance plot at low temperatures, such as that shown in Figure 4.4 (a), share a common value, reflecting the fact that these six Pt atoms form a hexagonal ring centred at the COM of the cluster, with each atom’s distance from the COM being equal.
Figure 4.4 (a), (b) and (c): USR comparison plots of atomic distance from COM at three different temperatures (a) 100 K (b) 770 K (c) 1800 K. Blue line represents a atomic distance profile of the structure at 0 K, while the black line is for atomic distances defined with respect to the temperature-dependent COM for current structure.
Figure 4.4 provide illustrative examples of COM atomic distance plots at different temperatures. The corresponding \( \text{Au}_{32}\text{Pt}_{6} \) structure for Figure 4.4 (a) at 100 K is shown in Figure 4.5 (a). The other two corresponding structures in Figure 4.4 for 770 K and 1800 K are also shown in Figure 4.5 (b) and (c) respectively. It is visually obvious that at a low temperature (as in the case of Figure 4.4 (a)), the USR graph has a rather regular, symmetrical and non-fluctuating profile. The black line effectively coincides with the blue line, implying the structure of the nanocluster at 100 K is highly similar to the reference structure at 0 K.

As temperature progressively increases [Figure 4.4 (b), (c)], the USR profiles display a corresponding increase in fluctuation and irregularity. These USR profiles provide a visually intuitive illustration about the statistical variation occurring in the structure of cluster during heating process.

Figure 4.4 (b) is the COM atomic distance plot obtained at temperature 770 K during the pre-melting stage. The slight fluctuations in the black line imply that the structure of the nanocluster become relatively irregular, and no longer remain similar to the reference structure. The platinum atoms no longer stay in hexagonal arrangement (which can be inferred from the observation that the y-value of the Pt atomic distances no longer shares a common value). However, the Pt atoms are still largely contained inside the shell made up of gold atoms. This can be inferred from the observation in the Figure 4.4 (b) profile, in which majority of the gold atoms stays above the blue reference plot, inferring that they are positioned further away from the COM, while most platinum atoms stay below.

Figure 4.4 (c) shows COM atomic distance plot obtained at temperature higher than the melting stage of the nanocluster (1800 K). Fluctuations in the black
line signify that uniform pattern of arrangement of gold atoms, in the form of a spherical shell, no longer persists. Moreover, many platinum atoms in the nanocluster at such a high temperature make their appearance in regions which were previously occupied only by shell atoms at low temperatures. The gold atoms, which used to stay above the blue reference line at low temperatures, now make many appearances below the line, signifying that they had penetrated the core region from outer shell. Overall, there is a non-negligible chance of occurrence whereby the platinum atoms are found further away than that gold atoms from the current COM.

COM atomic distance plots can provide further configurational information of a nanocluster at temperature all the way up to as high as one technically afford to simulate. In these extreme temperatures, the structure of a nanocluster loss their regular arrangement. For the case of Au$_{32}$Pt$_{6}$, it's default core-shell structure deteriorates as the temperature increases, such as that illustrated in Figure 4.4. A full list of all COM atomic distance plots at all temperatures simulated in this thesis, with COM as reference site, can be found in Appendix.

![Figure 4.5 (a), (b), (c): Structures of Au$_{32}$Pt$_{6}$ nanocluster with increasing temperature (a) 100 K (b) 770 K (c) 1800 K.](image)
The instantaneous distribution of all atoms in 3D space can be visually recognized in a MD simulation. However, to precise quantify these distributions consecutively along a lengthy, million frame MD trajectory, we need a good ‘measuring’ tool. To this end, COM atomic distance plots fit the bill as a very convenient and effective tool that can practically deliver the desired statistical information about the instantaneous relative atomic positions as compared to that in the 0 K reference structure. The melting mechanism of a core-shell structured binary cluster, such as that being investigated, can be revealed in a transparent manner with this USR measuring tool.

Other than COM, COM atomic distance plot can also be evaluated by using other types of reference site, i.e., CCM, FCM or FTF. As part of data collection tasks for this thesis, the USR code has been applied to produce plots for COM as well as that for other reference site. As it turns out, these COM atomic distance plots with difference type of reference sites all have similar appearances. The interpretations of the atomic movement of the \( \text{Au}_{32}\text{Pt}_{6} \) cluster at three different temperatures discussed in the previous paragraphs, where COM is assumed as the reference sites. To avoid over congestion of data presentation in this thesis, the COM atomic distance plots generated using CCM, FCM and FTF are not included despite their availability. However, the numerical data for all four types of USR reference sites are required to evaluate the similarity index, which is to be discussed in the next subsection.
4.5.1 Probability Distribution Function (PDF) of Similarity Index $P(\zeta)$

Quite independently from the COM atomic distance plots discussed in the previous subsection, the MD trajectory data were also post-processed (by using the USR code written by T.W. Yen) to abstract for another useful indicator, i.e., the similarity index – as discussed in Section 2.3 Ultrafast shape recognition. For every trajectory data (which has a fixed temperature), the USR code would calculate and record the shape similarity index $\zeta_i$ of the cluster at an interval of every 500 simulation steps. $i$ in the subscript refers to the index of time step in the MD trajectory. The USR code will then bin the shape similarity index collected $\{\zeta_1, \zeta_{501}, \zeta_{1001}, \ldots, \zeta_i, \ldots\}$ to form a normalised histogram with a pre-specified (and narrow) bin width. The histogram is known as the probability distribution function (PDF) of shape similarity index, denote $P(\zeta)$. In the following discussion the histogram will be approximated into the form of a continuous function. This approximated representation is feasible as the quantity of data collected $\{\zeta_1, \zeta_{501}, \zeta_{1001}, \ldots, \zeta_i, \ldots\}$, is huge. The graphs provide a wealth of statistical information about the dynamics of the atoms in the cluster during melting process. Interpretation of these plots will be done in the following discussion.

Consider Figure 4.6 which shows a family of $P(\zeta)$ plot for various temperatures, ranging from 100 K to 2000 K at a uniform but relatively coarse interval of 100 K. In low temperature regime, i.e., from $T = 100$ K to $T = 700$ K, the peaks fall consistently within the range of $0.90 \leq \zeta \leq 0.95$. This implies that the structures of the nanocluster at such temperature are still robust and similar to the reference structure. On the other hand, in large temperature regime, i.e., $T \geq 1100$ K, the curves are much lower, at around $\zeta = 0.50$. This indicates that the most probable
structure at this temperature range deviate quite significantly from the reference structure at $T = 0$ K.

For temperature ranges lying between the two temperature regimes mentioned above, i.e., from $T = 800$ K and $T = 1000$ K, several peaks can be seen in the corresponding curves, indicating a qualitative change was taking place in the thermal motion of structure. The phenomena responsible for such qualitative change is naturally interpreted as pre-melting and melting of the nanocluster. Once the temperature regime within which qualitative change in the structure of the nanocluster has been identified, MD simulation can then be performed with finer temperature resolution in this temperature regime. The detailed melting and pre-melting dynamics of the $\text{Au}_{32}\text{Pt}_6$ nanocluster, as revealed by the probability density function of shape similarity index, $P(\zeta)$, obtained by zooming into the $T = 800$ K and $T = 1000$ K regime will be presented in the following section.
Figure 4.6: Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $100 \text{ K} \leq T \leq 2000 \text{ K}$. 
4.5.1.(a) 100 K

A few cases from Figure 4.6 is selected for detailed interpretation in turn. First, consider the $T = 100$ K plots in Figure 4.6. Figure 4.7 and Figure 4.8 present the $P(\zeta)$ and COM atomic distance plots, side-by-side to the cluster structure taken at the same temperature. Most of the structures collected at this temperature were identical, as can be inferred from the sharp peak at $\zeta = 0.97$ in the $P(\zeta)$ plot, which spreads over a narrow range of $0.92 \leq \zeta \leq 0.96$, displaying a negatively skewed distribution as shown in Figure 4.7.

Figure 4.7: Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 100$ K.
Figure 4.8 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of Au$_{32}$Pt$_{6}$ nanocluster at $T = 100$ K.

The blue line in Figure 4.8 (a) represents the distances of the gold atoms from the COM in the reference structure while the blue circles mark the distances of the platinum atoms from the COM. These blue line and circles serve as a reference set in comparison with the black line and red circles which represent the distances of gold and platinum atoms from the COM respectively in the nanocluster at a particular temperature.

In Figure 4.8 (a), the COM atomic distance plot for $T = 100$ K (black line) coincides almost completely with the reference line (blue). So do the Pt-atom circles. This shows that the structures at this temperature are almost similar to the reference structure at 0 K.

4.5.1.(b) 400 K

Upon closer inspection on the $P(\zeta)$ plot in Figure 4.9, it can be inferred that vibrational motion of the atoms in the nanocluster at 400 K has become relatively
more violent, causing the statistical atomic distances to slightly shrink as compared to that at the 100 K. As a result, the structures at 400 K are statistically less identical to the reference structure than those at 100 K. This interpretation is based on the observation that the $P(\xi)$ plot becomes broader as compared to that at 100 K. The amplitude of the peak value, as well as the $\xi$ value at which the peak occurs, have also reduced.

Figure 4.9: Graph of $P(\xi)$ against $\xi$ for Au$_{32}$Pt$_6$ nanocluster at $T = 100$ K and 400 K.

Figure 4.10 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of Au$_{32}$Pt$_6$ nanocluster at $T = 400$ K.
The COM atomic distance plot for 400 K in Figure (4.10) (a) shows that the structure at this temperature is still similar to that of the reference structure. The slight fluctuations in the COM atomic distance plot is due to thermal vibration of individual atoms that causes variation in the structure along the MD trajectory. Overall, the geometrical configuration of the nanocluster remains statistically unchanged as compared to the reference structure.

4.5.1.(c) 700 K

As temperature continue to rise, the $P(\zeta)$ plot broadens and the peak shifted to a lower $\zeta$ value. More specifically, the peak shifts from 0.95 (at 400 K) to around 0.90 (at 700 K). The height of the peak in $P(\zeta)$ also decrease as $T$ increases from 400 K to 700 K. See Figure 4.11.

![Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_{6}$ nanocluster at $T = 400$ K and 700 K.]

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Figure 4.11: Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_{6}$ nanocluster at $T = 400$ K and 700 K.
Figure 4.12 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of Au$_{32}$Pt$_6$ nanocluster at $T = 700$ K.

The COM atomic distance plot for 700 K shows that the structure still differs slightly from that of the reference structure. Despite the minor irregularity, the nanocluster structure remains relatively indifferent from the reference structure.

4.5.1. (d) 800 K

As temperature rises further to 800 K, drastic change in the atom’s dynamics occurs, see Figure 4.13. The $P(\zeta)$ plot becomes stretched out along the horizontal direction while multiple peaks (at $\zeta \approx 0.45$, 0.60 and 0.90) with approximately equal heights but variable widths emerge. The $P(\zeta)$ plot is obviously qualitatively different from that at lower temperatures.

Interpreted statistically, the multiple peaks represent equal likelihood of possible structures with different similarity level to co-exist at this temperature. The possibility of detecting with good sensitivity a $P(\zeta)$ plot displaying multiple peaks of
equal or unequal height poses a new perspective in the study of cluster dynamics, as it offers a conveniently way to probe the existence of a possible pre-melting phase. A ‘perfect’ pre-melting phase is one in which all multi-peaks in the $P(\zeta)$ plot share a common height. As temperature continues to climb, one expects that the show of co-existence of equal-height peaks would become less prominent as the system gradually moves out of the pre-melting phase. However, as long as a multiple-peak pattern remains identifiable, irrespective of whether their heights are similar or otherwise, it signifies the persistence of the co-existence of configurations with different similarity index in the statistical samples at that temperature.

![Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 700$ K and 800 K.](image)

Figure 4.13: Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 700$ K and 800 K.
Figure 4.14 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of Au$_{32}$Pt$_6$ nanocluster at $T = 800$ K.

The structure of Au$_{32}$Pt$_6$ have changed utterly from the reference structure at 0 K, a fact that can be inferred from the violent deviation of the black line in the COM atomic distance plot of Figure 4.14 (a) from the reference plot (blue line). By visually monitoring the MD trajectory of the cluster using the MD visualization software VMD, it is observed that the 6 platinum atoms still largely remained in the core region. An illustrative configuration of the cluster at this temperature is as that displayed in Figure 4.14 (c). However, the default 2-dimension hexagon at lower temperature has turned into a 3-dimensional arrangement.

4.5.1.(e) Numerical Results in the 700 K - 800 K Region with Refined Temperature Resolution

The huge change in $P(\zeta)$ that occurs when temperature increases from 700 K to 800 K indicates that drastic transitions (perhaps also include pre-melting) must have occurred within this temperature range. As such, MD data with a finer
temperature resolution of 10 K were post-processed to provide finer details of the melting dynamics between 700 K and 800 K.

![Graph](image)

Figure 4.15: Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_{6}$ nanocluster at $T$ between 700 K and 800 K.

The results of the $P(\zeta)$ plots with a fine temperature resolution 10 K are presented in Figure 4.15. It shows that a qualitative change in the dynamics has occurred between 760 K to 770 K. The sudden appearance of a second peak at 770 K ($\zeta = 0.5$) (the red curve in Figure 4.15) suggests that the platinum hexagonal core has undergone a structural transition in this temperature range. The plots in Figure 4.15 allow us to pinpoint the pre-melting temperature of the Au$_{32}$Pt$_{6}$ nanocluster to 760 K – 770 K, which is considered an impressive precision in MD melting simulations. Thus, 760 K to 770K is considered as the temperature range for pre-melting phase of the Au$_{32}$Pt$_{6}$ nanocluster.
Figure 4.16: Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 760$ K and 770 K.

Figure 4.17 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of Au$_{32}$Pt$_6$ nanocluster at $T = 760$ K.
Figure 4.18 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of \( \text{Au}_{32}\text{Pt}_6 \) nanocluster at \( T = 770 \) K.

Figure 4.17 and Figure 4.18 present the COM atomic distance plots for \( T = 760 \) K and 770 K. The 760 K structure in Figure 4.17 (b) does not exhibit much difference from the reference structure. However, the structure had changed at 770 K (see Figure 4.18 (b)), where the six core platinum atoms have broken from the default configuration of a hexagon into a 3-dimensional structure. The saw-tooth shaped COM atomic distance plot, Figure 4.18 (a), shows that the average location of each atom is no longer similar as that at \( T = 760 \) K. Every single atom in \( \text{Au}_{32}\text{Pt}_6 \) has gained independence to move away from their default positions at low temperatures. Having said that, the Pt atoms are still largely contained within in the core region.

4.5.1.(f) 900 K

As the temperature continues to rise to 900 K from 800 K, the \( P(\zeta) \) plots display a trend in which the distribution of the multi-peaks undergoes a ‘flattening’ process, resulting in the disappearance of the subdominant ones while the
predominant one survives. As temperature increases consecutively in discrete steps, it can be visually observed from the series of the corresponding $P(\xi)$ plots that the subdominant peaks gradually sink, while the predominant peak gains in height concurrently due to the normalisation condition. The flattening of subdominant peaks can be interpreted as manifestation of the progress of diminishment in the pre-melting phase. However, in Figure 4.19, the multi-peak feature (which is still visible at $T = 800$ K) has not completely get wiped out at 900 K. Three identifiable peaks in Figure 4.19 infer the persistence of co-existence of three different configurations with a different $\xi$ (albeit with disparately different probabilities). The most probable structure at 900 K, which is indicated by the single prominent peak in Figure 4.19, occurs at $\xi \approx 0.60$, implying that even the most probably structure at 900 K is much less similar to the reference structure. As a comparison, the most probably structures before the pre-melting lie at around $\xi = 0.9$. The height of the single prominent peak at 900 K is suppressed to a much lower value of $P(\xi) \approx 0.035$ (as compared to $P(\xi) \approx 0.14$ during the on-set of pre-melting phase at $T = 760$ K, Figure 3.20) due to the severe flattening of the curve along the horizontal direction. The heights of the multi-peaks in a pre-melting $P(\xi)$ plot has to be scaled downwards to preserve the normalisation of the curve as its breadth spreads horizontally. Pre-melting has not yet completely ceased at $T = 900$ K.
Figure 4.19: Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 800$ K and 900 K.

Through visual inspection using VMD, it is observed that Au atoms did not stay put at their ‘default’ averaged distance from the COM. There is a tendency whereby Au atoms would swap positions among themselves. The Pt atoms were seen to be largely surrounded by Au atoms, and none of them shown significant likelihood to escape into the shell region. Probabilistically, the Pt atoms tend to be closer to the...
COM than most of the Au atoms in the nanocluster, maintaining the core-shell structure at $T = 900$ K.

4.5.1.(g) 1000 K

The $P(\xi)$ plots for temperatures $T = 900$ and 1000 K are shown in Figure 4.21. The most distinctive difference between the two plots is that the subdominant peaks that are visible in the 900 K plot have been completely flattened and are not discernible anymore at 1000 K. Only a single, widely broadened peak persisted at $\xi = 0.6$. The distinction implies that pre-melting behaviour of the nanocluster still persisted at 900 K but have ceased at 1000 K. This interpretation is based on the observation that the 1000 K curve does not display more than one distinctive peaks that are indicative of the existence of multiple probable structures with different $\xi$ at this temperature. Other than that, these two plots are similar in many aspects, including location of the predominant peak, skewness of the plot, and a large spread in the width of the curve. The overlapping of the peak’s location in these two plots (at $\xi = 0.6$) infers that in both temperatures the most probable structure is statistically similar.
Figure 4.21: Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 900$ K and 1000 K.

Figure 4.22 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of Au$_{32}$Pt$_6$ nanocluster at $T = 1000$ K.

From visual inspection using VMD, it is observed that the core shell structure of the nanocluster was still persisted at $T = 1000$ K. This observation is also consistent with the COM atomic distance plot in Figure 4.22 where most of the atomic distances of Pt atoms from COM are still lying below that of the Au atoms.
Comparing the $P(\zeta)$ plots for $T = 1000$ and 2000 K in Figure 4.23, it is seen that the location of the peak shifted from $\zeta = 0.60$ (for $T = 1000$ K) to $\zeta = 0.40$ (for $T = 2000$ K). In this temperature leap, the shape similarity index of the nanocluster deteriorates by 0.2. The structure of the nanocluster is less likely to be similar to the reference structure at temperature $T = 0$ K.

Figure 4.23: Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 1000$ K and 2000 K.

Figure 4.24 (a), (b) and (c): (a) Atomic distance comparison graphs obtained from USR and (b), (c) structure of $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 2000$ K.
When the MD trajectory for $T = 2000$ K is visualised via VMD, it is sighted that the core-shell structure disintegrates. The Pt atoms were no longer contained by surrounding Au atoms. Instead, some Pt atoms are seen to get distributed to distances further away from COM then the Au atoms. At such temperature, all the atoms in the nanocluster appeared to be arranged very disorderly. The nanocluster has melted and turned into random structure.

4.6 Comparison between Melting Post-Processing Techniques

After going through the melting process simulations using isothermal Brownian motion molecular dynamics, the data obtained are analysed using the specific heat capacity, Lindemann index and ultrafast shape recognition techniques. The sensitively of these techniques for detecting melting and pre-melting phases are now discussed. The following discussion refers to Figure 4.3 for the specific heat $C_v$ and Lindemann index $\delta$ curves.

At low temperatures, both specific heat $C_v$ and Lindemann index $\delta$ appear relatively flat and featureless. The $P(\zeta)$ plot has a unique sharp peak located at $\zeta = 1.0$ for $T = 0$ by definition, and approximately at 0.9 for $T = 100$ K.

Pre-melting signals at around 700 - 800 K are picked up by the $C_v$ and Lindemann index curves and manifest in the form of abrupt increment. Meanwhile, the $P(\zeta)$ plot displays a qualitative change in the curve skewness when going from 760 K to 770 K (see Figure 3.20). Concurrently, structural change is visually sighted at 770 K, where the 2D hexagon formed by core platinum atoms is destroyed and casted into a 3D configuration (but still contained within the core region). In this regards, the PDF of similarity index shows capability to pinpoint the occurrence of
pre-melting in this temperature range with impressive precision. On the other hand, the $C_v$ and Lindemann index curves have a rather ‘noisy’ signal at the vicinity of the pre-melting temperature, rendering the identification of pre-melting on-setting temperature less precise. The Lindemann index provides no clue at which temperature melting has occurred. On the other hand, the sharp peak in $C_v$ at $T = 1000 \text{ K}$ clearly marks the melting point, which is also precisely coincidental with the temperature at which complete flattening of subdominant peaks in the $P(\xi)$ curve occurs, marking the end of pre-melting phase. The above comparison provides a convincing case for the ultrafast shape recognition as a superior descriptor for monitoring cluster pre-melting and melting phenomena.

On the other hand, the USR code also provides statistical information on the COM atomic distance of each atom in a nanocluster, which is useful for quantitatively analysing the detailed structural change (from core-shell to random structure) during the melting process. In the above interpretations presented for each temperature, the state of core-shell structure is only manually recognized and visually identified via visualisation software.

4.7 Further Verification For Ultrafast Shape Recognition

In this section, another system is to be simulated, namely the Au$_{38}$ cluster. The purpose to do so is two-fold: To investigate the thermal stability of the cluster, which is a special case of the Au-Pt cluster with zero Pt atom, and (2) to use Au$_{38}$ as another test case to independently justify the use of USR method for identification of pre-melting and melting phases in a nanosystem. To this end, the calculation
procedures as applied to the $\text{Au}_{32}\text{Pt}_6$ cluster in previous sections will be repeated on $\text{Au}_{38}$.

### 4.7.1 Ground-State Structure for $\text{Au}_{38}$

The ground-state of 38-atom pure gold nanocluster has a core-shell structure, hence is suitable as a candidate for verifying the data of $\text{Au}_{32}\text{Pt}_2$ which was post-processed via the USR approach. Based on the result obtained from PTMBHGA, the lowest-energy structure for 38-atom gold nanocluster has a shape of a truncated octahedron with $O_h$ symmetry and symmetry order 48, see Figure 5.1.

![Figure 4.25: Ground-state structure for 38-atom gold nanocluster.](image)

The outer surface of this truncated octahedron structure consists of 32 gold atoms while the inner core of this structure is made up of 6 gold atoms forming an octahedron.

### 4.7.2 Melting Process

The study of melting process for $\text{Au}_{38}$ cluster begins with the BTIMD simulation. The resultant MD trajectory data is then post-processed to attain the specific heat $C_v$ and Lindemann index curves, as displayed in Figure 5.2.
Figure 4.26: Specific heat $C_v$ and Lindemann index plot for Au$_{38}$. The dotted line is for Lindemann index.

Referring to the $C_v$ curve, a drastic change appears at around 550 K. This shows that the pre-melting occurs at that temperature. The abrupt rise in the $C_v$ curve at 550 K is seen to coincide with a similar rise in the Lindemann index curve. These abrupt changes indicate a structural change is occurring around the vicinity of this temperature. Due to the fluctuations in the shape of these curves at this temperature range, it is not feasible to determine reliable details about the precise pre-melting temperature of the Au$_{38}$. In addition, it is not clear from these curves at which precise temperature melting of the cluster is occurring. To do so, USR method is used.

4.7.3 Ultrafast Shape Recognition for Au$_{38}$

USR post-processing procedure is carried out after the $C_v$ and Lindemann curves are obtained. The collection of all PDF of shape similarity index $P(\xi)$ is presented in Figure 4.27, spanning a temperature range of $100 \, \text{K} \leq T \leq 2000 \, \text{K}$. At
lower temperature, the peaks in $P(\zeta)$ are located at $\zeta$ valued around 0.95, proving that the simulated structures for 38-atom gold cluster are mostly identical to the reference structure (at 0 K). When temperature grows within the range of 100 K to 600 K, the peak shifts incrementally towards a smaller value of $\xi \approx 0.92$. A qualitative change occurs to the $P(\xi)$ plot when the temperature passes from 600 K to 700 K. To show further details, a new temperature $T = 550$ K is introduced into the graph to reveal a more refined detail in this temperature interval. As shown in Figure 4.28, the 550 K plot displays the emergence of multiple peaks, which are absent in the 500 K plot. This is a clear signature of co-existence of multiple probable structures. Hence, 550 K is identified, as the on-set temperature of pre-melting phase in the Au$_{38}$ cluster with a temperature resolution of $\Delta T = 50$ K. Figure 4.29 shows an example of a probable structure found at 550 K. The truncated octahedron shape has been distorted, hence resulting in a reduced value of its shape similarity index $\zeta$. The end of pre-melting phase can be similarly obtained by comparing the $P(\zeta)$ plots between two consecutive temperatures with a temperature resolution $\Delta T$ in turn until the multiple subdominant peaks are completely flattened, leaving only a broadened and suppressed, predominant peak which is located at a much lower $\zeta$ value.

This finding proves the consistency of USR as a detailed post-process method to study the melting mechanism of nanoclusters.
Figure 4.27: Graph of $P(\zeta)$ against $\zeta$ for Au$_{38}$ nanocluster at $100 \, \text{K} \leq T \leq 2000 \, \text{K}$. 
Figure 4.28: Graph of $P(\zeta)$ against $\zeta$ for Au$_{38}$ nanocluster at $T = 500$ K and 550 K.

Figure 4.29: Structure for 38 gold nanocluster at $T = 550$ K.
CHAPTER 5

CONCLUSION AND FUTURE STUDIES

5.1 Conclusion

The PTMBHGA code, which was created and made available to us by S. K. Lai’s research team from NCU Taiwan, has been used to determine the ground-state structure of the subjects of interest in this research, which is the 38-atom gold-platinum nanoclusters for all compositions. The PTMBHGA code, which has included a built-in Gupta force field library for many atomic species, has been proven to be very computationally effective, practical and reliable to produce robust ground-state structures of the clusters investigated in this thesis. In this thesis, the ground-state structures of pure gold and pure platinum clusters with size from 3 to 55 atoms were obtained with the PTMBHGA code. Table 3.2 and 3.4 display these results, along with their symmetric properties. The relative stability of these pure clusters was also analysed by plotting the second energy difference of these clusters as a function of size. It was found that for the pure gold cluster, the cluster with highest relative stability is that with size \( N = 13 \) atoms, and a \( I_h \) symmetry structure. In the case of pure platinum cluster, the cluster with highest relative stability is that with size \( N = 13 \) atoms and a \( I_h \) symmetry structure. In this thesis, a good amount of effort has been spent to generate, using the PTMBHGA code, the ground state structures of the binary alloy \( \text{Au}_n\text{Pt}_{38-n} \) cluster for \( n \) ranging from 0 to 38. Highly stable gold-platinum nanoclusters, namely that with gold composition \( n = 25, 30 \) and
32, were identified, along with their symmetry properties. All of the $\text{Au}_n\text{Pt}_{38-n}$ ground-state structures found display core-shell structure, in which all of the Pt atoms in the cluster are surrounded by Au atoms, which distances from the centre-of-mass (COM) are larger than the Pt’s.

Due to its high stability and interesting core-shell segregation structure, nanocluster with 32 gold and 6 platinum atoms has been specifically selected as the subject of further investigation, in which its melting behaviour was scrutinized via computational simulations. Another sample system, $\text{Au}_{12}\text{Cu}_1$, was also simulated for the purpose of comparison with published results in the literature, Yen et al., 2009, which was also calculated using the same PTMBHGA code. The results of $\text{Au}_{12}\text{Cu}_1$ calculated in this thesis agrees well with that by Yen et al., 2009. Melting in clusters is a phase-changing phenomena induced by temperature. Brownian type isothermal molecular dynamics simulation (BTIMD) was the tool deployed to simulate the melting process of $\text{Au}_{12}\text{Cu}_1$ and $\text{Au}_{32}\text{Pt}_6$ for temperature ranging from 100 K to 2000 K. The MD trajectories from the simulations were post-processed to first obtain the specific heat $C_v$ and Lindemann index of the simulated nanoclusters. Specific heat capacity was computed in the MD context as the fluctuation in energy, while Lindemann parameter fluctuation was the averaged distances among the atoms in the system. The $C_v$ and Lindemann curves for $\text{Au}_{32}\text{Pt}_6$ denoted a fuzzy signal of pre-melting phase at around 700 K to 800 K. A relatively sharp melting peak at around 1000 K was also displayed in the $C_v$, but no clear, identifiable feature was seen in the Lindemann curve to indicate melting.

Pre-melting of the 38-atom nanocluster involves a 2-D to 3-D structural transition in the core platinum atoms, which formed a hexagon at low temperatures. The gold atoms still remained in the shell until around 1000 K where some platinum
atom began to shift into the outer shell, which was statistically only occupied by Au atoms at low temperature. The process of observing the structural changes via VMD visualisation is time consuming, and only qualitative information can be gained. A statistical approach of analysing the data obtained for thermally-induced structural transition would be desired. This led to the introduction of a relatively novel measuring tool, the Ultrafast Shape Recognition (USR) approach. The USR operates on a statistical basis. At any given fixed temperature, a huge amount of shape similarity index $\xi_i$ was recorded along a MD trajectory. They were binned into a histogram, then normalised and approximated into a continuous curve $P(\xi)$, known as probability density function (PDF) of shape similarity index. Using the $P(\xi)$ plot as a measuring tool, it was found that the pre-melting in the Au$_{32}$Pt$_6$ cluster happened within 760 K to 770 K. This conclusion was arrived at by comparing the $P(\xi)$ plots at both temperatures, as shown in Figure 4.16. There, it was observed that the 770 K plot skewed to the right. Apart from the predominate peak near $\xi \approx 0.9$, the plot displayed an emergence of a few subdominant peaks which were broad, suppressed in height, and located at disparately distinct $\xi$. These subdominant peaks inferred the co-existence of other statistically probable structures within the Au$_{32}$Pt$_6$ at these $\xi$ values. Comparing the $P(\xi)$ curves for two temperatures separated by a resolution $\Delta T$ in the pre-melting region allows one to pinpoint the temperature at which the pre-melting phase ceased. This happened as shown in Figure 4.21, where the subdominant peaks as seen in the 900 K $P(\xi)$ plot became flattened at 1000 K, where only a broadened, height-suppressed, dominant peak left. The complete flattening of subdominant peaks at 1000 K marked the end of pre-melting phase in Au$_{32}$Pt$_6$, a remarkably precise information that was able to get picked up by the $P(\xi)$ plots. Quite independently, the collection of atomic coordinates was also used
to produce another graph, namely, the COM atomic distance plot. It was calculated based on the distance of each atom, $d$ (in Angstrom) with respect to the centre of mass (COM) of current structure in a time step $i$. The resultant curve of $d$ against number of atom, $n$, is known as the COM atomic distance plot. There was one COM atomic distance plot for each fixed temperature. The shape of a COM atomic distance plot allows one to gauge in a quantitative manner how far the $\text{Au}_{32}\text{Pt}_6$ cluster deviates from the ideal core-shell structure as that of the reference cluster at 0 K. There was a temperature range (i.e., from 760 K to 770 K) where the Pt atoms in the hexagon broke into 3D configurations, yet the cluster, as a whole, still statistically maintained a core-shell segregation. As temperature continued to increase exceeding 2000 K, the cluster completely melted, and the core-shell segregation was completely destroyed into random structure. Au$_{38}$ clusters had been further investigated to verify the consistency of ultrafast shape recognition technique and the proof of pre-melting occurred at around temperature $T = 550$ K.

5.2 Future Studies

The ultrafast shape recognition technique can applied into other fields besides determining the thermal properties of nanoclusters. Besides, it can be improved by taking into account more statistical information into the USR code. For future studies in this topic, the post-processing method can be enhanced by producing a structural index curve that provides a quantitative picture of how the state of the core-shell segregation evolve as a function of temperature in the nanocluster.
LIST OF PUBLICATION


REFERENCES


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