Thermal Properties and Ground-state Structures of Pure and Alloy Nanoclusters via Molecular Dynamics Simulations

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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 for various composition via PTMBHGA. Bimetallic nanocluster Au_{32}Pt_6 with D_{6h} symmetry has been selected as the nanocluster for further investigation in the thermal properties as it is the most stable bimetallic nanocluster studied in this thesis. The melting mechanism used in this research is BTIMD.
ABSTRACT

• Specific heat, $C_v$, and Lindemann index, $\delta$ served as the common descriptor used to monitor the melting behaviour of $\text{Au}_{32}\text{Pt}_6$ nanoclusters. Both $C_v$ and $\delta$ curves showed the presence of pre-melting phase in nanoclusters. To further investigate the pre-melting stage, USR has been introduced. The data was plotted into atomic-distance plots and probability distribution function of shape similarity index.

• The three methods shown agreed with each other in determining the pre-melting and melting range of nanoclusters. However, the USR method had provided detailed insight to the melting behaviour of nanoclusters and proven itself to be a more precise as indicator.
1. Introduction
   ◦ Importance of nanoclusters
   ◦ Problem statements

2. Theoretical Background & Methodologies
   ◦ Structural properties of nanoclusters
   ◦ Thermal properties of nanoclusters
   ◦ Ultrafast shape recognition

3. Results & Discussions
   ◦ Ground-state structures of nanoclusters
   ◦ Commonly used post-processing methods
   ◦ Post-processing with ultrafast shape recognition

4. Further Verification for Ultrafast Shape Recognition

5. Conclusion
INTRODUCTION

Nanoclusters

• A group of particles (atoms or molecules) with its size in the order of nanometer (10-9 m) formed by any countable number of atoms that are combined together.

• Nanoclusters can be formed from identical atoms (homo-atomic) or two or more types of atoms (hetero-atomic).

• Each type of clusters has their own uniqueness that make them a worthwhile topic to study.

• Their physical properties generally display a size-dependence behaviour, thus nanoclusters of different sizes will exhibits different properties despite being formed by the same elements.
INTRODUCTION

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.

• 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.

• 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.
INTRODUCTION

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).
- Platinum (Pt) is a transition element in periodic table with atomic number 78. It is an important catalyst in various industries.
- 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).
- 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).
PROBLEM STATEMENTS

• In order to know how gold-platinum nanoclusters are affected by temperature variation, we shall study their possible structures at high temperatures, and they are altered, as well as the melting behaviour of these nanoclusters.

• 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 detailed mechanism of structural change during the pre-melting phases.

• Quantifying the detail mechanism of structural change in nanoclusters during pre-melting phases is essential to understand the changes that occur within the nanocluster as temperature varies.

• A novel approach is proposed to quantify and capture these details.
THEORETICAL BACKGROUND AND METHODOLOGIES

Parallel Tempering
Multicanonical Basin
Hopping plus Genetic
Algorithm

Brownian type
Isothermal Molecular
Dynamics

Ultrafast Shape
Recognition
STRUCTURAL PROPERTIES OF NANOCLUSTERS

Parallel Tempering Multicanonical Basin Hopping plus Genetic Algorithm (PTMBHGA)

Gupta many body potential

- To calculate the interactions between many-body atoms.
- Gupta parameters for gold, platinum and gold platinum atoms.

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PTMBHGA

Start

Generate:
20 random configurations

Perform:
100 BH steps
10 MBH steps

Repeat BH steps with 20 and 30 MBH steps respectively

Perform:
500 generations of GA

Determine lowest potential energy & configurations of nanocluster

Stop
THERMAL PROPERTIES OF NANOCLUSTERS

Brownian type isothermal molecular dynamics simulation

• 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).

• Throughout all simulations, time step of $\Delta t$ which is fixed between $1 \times 10^{-15}$ to $5 \times 10^{-15}$ s was used.

• $(T \leq 500 \text{ K})$, $1 \times 10^8$ steps were performed 
$(550 \text{ K} \leq T \leq 1050 \text{ K})$, $2 \times 10^8$ steps were performed 
$(T \geq 1100 \text{ K})$, $2 \times 10^7$ steps were performed.

• 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 $700 \text{ K} \leq T \leq 1050 \text{ K}$, a more refined interval of 10 K is adopted.
ULTRAFAST SHAPE RECOGNITION

- Molecular shape recognition technique is widely applied in chemistry field to categorize molecular structures, especially proteins structure.

- The idea of USR ideology has been inspired S. K. Lai’s team from National Central University, Taiwan.

- 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 0K 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 $i = 0$. 
ULTRAFAST SHAPE RECOGNITION

• 4 different statistical moments, based on the 3D spatial coordinates of the atoms:
  o Mean value
  o Variance
  o Skewness
  o Kurtosis

• These moments in turns can be calculated by referring to 4 different reference sites:
  o Centre of mass (COM)
  o Atom closest to the centre of mass (CCM)
  o Atom farthest from the centre of mass (FCM)
  o Atom farthest to atom farthest from the centre of mass (FTF)

• Hence, overall, 16 different statistical moment descriptors can be discerned.
RESULTS AND DISCUSSIONS
GROUND-STATE STRUCTURES OF NANOCLUSTERS

Gold nanoclusters

The comparison between the structures of gold nanoclusters obtained from PTMBHGA (left) and reference (right) from Xia Wu et al. 2012.
GROUND-STATE STRUCTURES OF NANOCLUSTERS

**Second energy difference**

- An indicator to monitor the relative stability of nanoclusters.
- A large value at a particular cluster size in second energy difference plot implies higher relative stability compared to neighbouring cluster sizes.

The second energy difference plot for gold nanoclusters from size 3-55 atoms.
GROUND-STATE STRUCTURES OF NANOCLUSTERS

Platinum Nanoclusters

The second energy difference plot for platinum nanoclusters from size 3-55 atoms.
Ground-state Structures of Nanocluster

Gold-platinum Nanoclusters

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 \( \text{Au}_n\text{Pt}_{38-n} \).
Ground-state Structures of Nanocluster

$\text{Au}_{32}\text{Pt}_6$

Ground-state structure for $\text{Au}_{32}\text{Pt}_6$ nanocluster
MELTING BEHAVIOUR OF NANOCLUSTERS

Specific Heat, $C_v$
- 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.
- $C_v$ is the measure of energetic changes

Lindemann Index, $\delta$
- The second indicator used in this thesis to quantify the melting behaviour of the clusters is Lindemann index which also a common tool used to study variation in geometrical properties of a nanocluster in a thermal process.
- $\delta$ is the measure of structural change
MELTING BEHAVIOUR OF NANOCLUSTERS

Test Case: \( \text{Au}_{12} \text{Cu}_{1} \)

(Left) Specific heat \( C_v \) and (Right) Lindemann Index \( \delta \) against temperature for \( \text{Au}_{12} \text{Cu}_{1} \) obtained by Yen et al., 2009.
Graph of specific heat $C_V$ (continuous line) and Lindemann Index $\delta$ (dotted line) against temperature for $\text{Au}_{32}\text{Pt}_6$ nanocluster.
MELTING BEHAVIOUR OF NANOCWATCHERS

Post-Processing with Ultrafast Shape Recognition

USR code was used to produce two types of statistical data useful for analysing the melting mechanism:

• **Atomic-distance plot**
  
  - 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.
Post-Processing with Ultrafast Shape Recognition

USR code was used to produce two types of statistical data useful for analysing the melting mechanism:

- **Probability of Similarity Index** $P(\zeta)$
  
  - 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.
  
  - The USR code will then bin the shape similarity index collected $\{\zeta_1, \zeta_{501}, \zeta_{1001}, ..., \zeta_i, ...\}$ to form a normalised histogram with a pre-specified (and narrow) bin width.
Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_6$ nanocluster at $100 \text{ K} \leq T \leq 2000 \text{ K}$
MELTING BEHAVIOUR OF NANOCLUSTERS

Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 100$ K

Atomic distance comparison graphs obtained from USR and structure of $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 100$ K
MELTING BEHAVIOUR OF NANOCCLUSTERS

Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 100$ K

Atomic distance comparison graphs obtained from USR and structure of $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 100$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

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

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 400$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

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

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 400$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

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

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_{6}$ nanocluster at $T = 700$ K
Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 400$ K and $700$ K

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 700$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

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

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 800$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

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

Atomic distance comparison graphs obtained from USR and structure of $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 800$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_6$ nanocluster at $700 \text{ K} \leq T \leq 800 \text{ K}$
Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 760$ K and 770 K
MELTING BEHAVIOUR OF NANOCLUSTERS

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 760$ K

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 770$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 800$ K and $900$ K

Atomic distance comparison graphs obtained from USR and structure of $\text{Au}_{32}\text{Pt}_6$ nanocluster at $T = 900$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 800$ K and 900 K

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 900$ K.
MELTING BEHAVIOUR OF NANOCLUSTERS

Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 900$ K and 1000 K

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 1000$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

Graph of $P(\zeta)$ against $\zeta$ for Au$_{32}$Pt$_6$ nanocluster at $T = 900$ K and 1000 K

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T' = 1000$ K
MELTING BEHAVIOUR OF NANOCLUSTERS

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

Atomic distance comparison graphs obtained from USR and structure of Au$_{32}$Pt$_6$ nanocluster at $T = 2000$ K
Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{32}\text{Pt}_{6}$ nanocluster at $T = 1000$ K and 2000 K.

Atomic distance comparison graphs obtained from USR and structure of $\text{Au}_{32}\text{Pt}_{6}$ nanocluster at $T = 2000$ K.
FURTHER VERIFICATION FOR USR

The purpose to do so:
• To investigate the thermal stability of the cluster, which is a special case of the Au-Pt cluster with zero Pt atom.
• 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.

The calculation procedures as applied to the Au$_{32}$Pt$_6$ cluster in previous sections will be repeated on Au$_{38}$

Ground-state structure for 38 atoms gold nanocluster
FURTHER VERIFICATION FOR USR

Specific heat $C_v$ and Lindemann index plot for $\text{Au}_{38}$. The dotted line is for Lindemann index.
FURTHER VERIFICATION FOR USR

Graph of $P(\zeta)$ against $\zeta$ for $\text{Au}_{38}$ nanocluster at $100 \text{ K} \leq T \leq 2000 \text{ K}$
FURTHER VERIFICATION FOR USR

Graph of $P(\zeta)$ against $\zeta$ for Au$_{38}$ nanocluster at $T = 500$ K and 550 K

Structure for 38 gold nanocluster at $T = 550$ K
CONCLUSION AND FUTURE STUDIES

• In this thesis, the ground-state structures of pure gold and pure platinum clusters with size from 3 to 55 atoms and the ground state structures of the binary alloy $\text{Au}_n\text{Pt}_{38-n}$ cluster for $n$ ranging from 0 to 38 were obtained with the PTMBHGA code, which was created and made available to us by S. K. Lai’s research team from NCU Taiwan.
• The relative stability of these pure clusters was also analysed by plotting the second energy difference of these clusters as a function of size.
• For both pure gold and platinum cluster, the cluster with highest relative stability is that with size $N = 13$ atoms, and a $I_h$ symmetry structure.
• 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.
CONCLUSION AND FUTURE STUDIES

• 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 investigation, in which its melting behaviour was scrutinized via computational simulations.

• Brownian type isothermal molecular dynamics simulation (BTIMD) was the tool deployed to simulate the melting process of Au\textsubscript{12}Cu\textsubscript{1} and Au\textsubscript{32}Pt\textsubscript{6} for temperature ranging from 100 K to 2000 K.

• Au\textsubscript{12}Cu\textsubscript{1}, was also simulated for the purpose of comparison with published results in the literature, Yen et al., 2009, that was calculated using the same PTMBHGA code. The results of Au\textsubscript{12}Cu\textsubscript{1} calculated in this thesis agrees well with that by Yen et al., 2009.

• The MD trajectories from the simulations were post-processed to 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 Au\textsubscript{32}Pt\textsubscript{6} denoted a 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.
CONCLUSION AND FUTURE STUDIES

• In order to simplify the process, Ultrafast Shape Recognition (USR) approach was introduced. The USR operates based on a statistical basis. The post-processing began by recording the atomic coordinates of each atom in all MD steps at a fixed temperature.

• A total of 16 statistical moments could be calculated from these coordinates in any given time step. These statistical moments in each time step $i$ were then used as input to obtain the numerical value of a descriptor known as shape similarity index, $\xi_i$ (with the condition $0 \leq \xi_i \leq 1$). Similarity index measured the degree of similarity of the structure at an instantaneous MD step $i$ to that of a reference structure, which was defined as the ground-state structure at 0 K.

• At any given fixed temperature, a huge amount of $\xi_i$ was recorded along a MD trajectory. They were binned into a histogram, then normalised and approximated into a continuous curve $P(\xi)$. Using the $P(\xi)$ plot as a measuring tool, it was found that the pre-melting in the $\text{Au}_{32}\text{Pt}_6$ cluster happened within 760 K to 770 K.

• Quite independently, the collection of atomic coordinates was also used to produce another graph, namely, the atomic-distance plot. 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.
CONCLUSION AND FUTURE STUDIES

• The ultrafast shape recognition technique can be applied into other fields besides determining the thermal properties of nanoclusters. It can be improved with applying some statistical method added into the USR code.

• For future studies in this topic, the post-processing method can be enhance by produce 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.
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