Molecular Dynamics Study of Extraordinary Elastic Deformation Found in Gold Atomic Cluster*

Ken-ichi SAITO** and Yoshiaki YONEKAWA***
** Department of Mechanical Engineering, Faculty of Engineering Science, Kansai University
3–3–35 Yamate-cho, Suita, Osaka 564–8680, Japan
E-mail: saitou@kansai-u.ac.jp
*** Graduate School of Engineering, Kansai University
3–3–35 Yamate-cho, Suita, Osaka 564–8680, Japan

Abstract
Inelastic deformation of gold (Au) atomic cluster is investigated by using molecular dynamics (MD) simulations. We performed compression and unloading tests in which silicon (Si) plates approach each other and push single Au cluster of 4 nm diameter in between. Possibility of super-elastic (hyper-elastic) behavior is first discussed in the present study. The potential function of embedded atom method is adopted inside Au cluster, whereas other interactions are formulated by simplified Lennard-Jones interaction. The cluster in MD simulation shows large recovery strain which is reversible in unloading process after compression. The recovery strain is estimated on average from 5 to 10%. It is found that there are deformation mechanisms depending on temperature of the cluster. Mechanism for low temperature is based on slip motion and that for high temperature is dominated by surface reconstruction. The strength of interaction energy between Si plate and the Au cluster which may cause pulling force and produce tensile state is investigated, referring to our AFM experiment.

Key words: Numerical Simulation, Atomic Cluster, Molecular Dynamics, Nanomaterial, Plasticity, Superelasticity, Gold, Strain

1. Introduction
Atomic cluster is a typical nano-sized material, which is composed of only several tens to thousands of atoms. It has been well studied that atomic cluster shows extraordinary behavior with regard to electronic, magnetic or quantum properties. Such behavior is caused by confining a few number of valence electrons inside the atomic aggregate. As for structural properties, similarly, it is well known that an atomic cluster shows tremendous drop of melting temperature(1). Crystalline structures of many metallic clusters take anomalous icosahedron or decahedron shape. These structural properties peculiar to atomic clusters are quite different from those in a bulk material with ordinary dimension and it is supposed that they are caused by large ratio of surface atoms. Peculiarity in mechanical response to external loading has been found in many studies concerning atomic clusters. For example, a "C60 fullerene" was compressed by external loading up to one third of original size and, nevertheless, it recovered its natural shape by unloading(2). Furthermore, interesting behavior in coalescence or rupture between atomic clusters which are composed of transition metals is extensively studied(3)–(5). Recently, researchers found that two nano-sized Lennard-Jones (LJ) clusters shows anomalous "super-rebound" behavior when they collide each other in thermally activated state(6). The "super-rebound" means that relative outbound velocity becomes higher than inbound one. It seems to violate the law of dynamics, but it is understood that this could happen because they are small and have only the small number of degrees of freedom. Other research was focused on crystalline change in melting or solidification of a gold cluster(1). Reviewing these
previous studies, the nano-sized materials generally shows very large deformation in loading. Since mechanical response of atomic cluster is strongly affected by surface atoms which have larger energy, it is guessed that the behavior is completely different from that of bulk state. Therefore, large recovery of shape in atomic cluster is expected in unloading process.

Usually, the sum of free energy mostly distributed over surface atoms is going to be minimized by relaxation of atomic structure (called surface relaxation). At the same time, the overall shape will be reconstructed so that the free energy is diminished if it is allowed. A good analogy for this is found in liquid droplet which always recover a spherical geometry as a result of minimizing area, energy or tension of the surface. Therefore, we can expect an atomic cluster to recover its original (spherical) shape even after it has conducted large deformation. Then, large recovery of shape which will be seen in an atomic cluster should be in the domain of super-elastic materials (super-elasticity). Of course, however, the super-elastic effect will be successful only if the ordinary deformation mechanisms in solid, such as crystalline slip, dislocation or twin deformation, is inactivated or incompletely activated.

In the previous experiment with TEM observation, a single gold (Au) atomic cluster with 4 nm diameter, which is put in between silicon (Si) substrates, was successfully compressed. The cluster is subjected to a large amount of uniaxial strain, but with separating substrates the cluster reveals very large recovery of shape\(^7\). That study investigated unique initiation of deformation twins as well as shape change. Thus, referring this curious experiment, in this paper, we are going to show numerical results and discuss the super-elastic deformation mechanism of Au atomic cluster. The methodology is molecular dynamics (MD) simulation where compression test and unloading process are performed. To the authors’ knowledge, there has not been, so far, any intensive study which focuses on such super-elastic mechanism of atomic cluster by means of MD simulation. The advantage of MD modeling and simulation would be found in varying conditions and understanding atom-by-atom behavior.

In the present study, we will derive the potential ability of Au cluster. Besides, we are going to discuss sensitivity to temperature condition. Also, in the present MD modeling, interatomic potential between Au and Si is crucial. Therefore, we are attempting to include our experimental data concerning adhesive force between Au and Si atoms which is obtained in atomic force microscopy (AFM) measurements. Moreover, in order to estimate the cluster shape, we introduce a continuum concept of strain tensor.

It is true that the size of cluster is one of important factors for super-elasticity, yet we leave the investigation in further studies. Consequently, we concentrate one size of Au cluster in the present paper. Besides, the variety in the depth and speed of compression (strain rate) will be of much interest but be left for further studies. The authors believe that by verifying a basic evidence of super-elasticity in small gold cluster, it leads to an innovation of more flexible fixing mechanism applicable to micromechatronics for information and precision engineering.

This paper is organized as follows. First, MD modeling is shown, where the potential model of Au cluster and Si substrates or computation conditions are shown. Subsequently, the results are shown and discussions are made. Finally, we arrive at conclusion of our study.

2. Theory and Computation Model

2.1. Computation model for molecular dynamics simulations

First, we begin with the molecular dynamics (MD) simulation model that we use. Figure 1 shows the present MD computation model, in which a single cluster made up of 2093 Au atoms and assembled in sphere of 4.08 nm diameter. The cluster is to be compressed by Si plates located top and bottom with relative velocity, \(V=35\) m/s. Starting with the perfectly regular f.c.c. lattice, the initial atomic configuration for loading has accomplished thermal equilibration at an objective temperature \(T\). Since there is no mechanical constraint on the atomic cluster before it is caught by Si plates, the whole body rotates slightly. Crystalline structure inside after equilibration is recognized as almost f.c.c. structure. All of these con-
sequences are regarded as natural appearance of the cluster. On the other hand, Si atoms contained in substrates located at top and bottom in y direction are fixed at the regular point and each plates are treated as rigid body throughout the MD simulation. As will be mentioned later, atomic positions of Si are aligned in f.c.c. lattice. The initial distance between surfaces of Au cluster and Si substrate is 2 nm, which is nearly half of cluster radius and is more than interacting range. Temperature of the system is controlled by using velocity scaling method, so as to keep a certain value (ranging from 0 to 800 K). Table 1 summarizes the conditions of the present MD model.

![Molecular dynamics computation model of gold (Au) cluster](image)

**Table 1** Computation conditions and potential parameters

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Au / Si)</td>
<td>nm</td>
<td>0.408 / 0.543</td>
</tr>
<tr>
<td>Diameter of cluster</td>
<td>nm</td>
<td>4.08</td>
</tr>
<tr>
<td>The number of atoms (Total / Au cluster / Si atoms)</td>
<td></td>
<td>7569 / 2093 / 5476</td>
</tr>
<tr>
<td>LJ parameter (r_{ij}(\text{Si-Si / Si-Au}))</td>
<td>nm</td>
<td>0.342 / 0.300</td>
</tr>
<tr>
<td>LJ parameter (\varepsilon_{ij}(\text{Si-Si / Si-Au}))</td>
<td>10^{-20}</td>
<td>6.20 / 1.32 / 0.85 / 0.40</td>
</tr>
</tbody>
</table>

2.2. Interatomic potentials

The interatomic potential for Au-Au interaction is an embedded atom method (EAM) which is proposed by Cai et al.\(^8\). This potential is developed for alloy systems of metallic elements (Al, Au, Ag, Cu, Ni, Pd, Pt) and provides reliable energies for their surface and defect structures. The reader can refer to the original work about the detail\(^8\).

Since the present interest is structural change of Au atomic system, the melting point \(T_m\) in using this EAM potential is preliminarily evaluated. We examine \(T_m\) for cluster’s configuration with 4.08 nm diameter \((N = 2093)\) as well as bulk state of Au crystal with almost the same size. The MD simulations for \(NVT\) or \(NPT\) ensemble are conducted by elevating temperature \(T\) (the range is from 0 to 4500 K) with constant gradient, \(dT/dt = 1.875 \times 10^{12} \text{K/s}\). The results are shown in Table 2. \(T_m\) is marked when drastic increase appears in potential energy of the bulk system in \(NVT\) ensemble. In \(NPT\) ensemble or cluster’s case, it is done when radical increase is found in volume of the bulk system or cluster’s body. The estimated \(T_m=1350\) K for bulk \((NPT)\) agrees well with experimental value of 1337 K. This means that this EAM potential is fully reliable for solid-liquid phase change. In addition, it is interesting that \(T_m\) of the cluster in the present use is diminished down to 64~50% of the bulk value.

On the occasion of MD modeling of Si plates, we need to use some approximations. Si atoms are aligned in f.c.c. lattice, omitting usual diamond structure (but, lattice constant is
Table 2  Estimated melting temperature \( T_m \) of Au crystal; for cluster configuration and bulk state, with gradient \( 1.875 \times 10^{12} \) K/s

<table>
<thead>
<tr>
<th>Condition</th>
<th>( T_m ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk state (NVT)</td>
<td>3040</td>
</tr>
<tr>
<td>bulk state (NPT)</td>
<td>1350</td>
</tr>
<tr>
<td>Cluster configuration ((N = 2093))</td>
<td>650–860</td>
</tr>
<tr>
<td>Experimental value</td>
<td>1337.33</td>
</tr>
</tbody>
</table>

adjusted by density of silicon). The Si-Si interaction is expressed by Lennard-Jones (LJ) type, as shown in Eq.(1). Of course, compared with the approach using precise first-principle calculation\(^9\), approximating atomic interaction by LJ type seems quite crude. But, advantage of LJ potential is that it is simple and it exhibits both attractive and repulsive interaction required for the present compressive test. The cohesive energy \( e_{LJ,\text{Si-Si}} \) is fitted for experimental data of Si crystal assuming the coordination number of f.c.c.(=12).

\[
\phi(r) = 4e_{LJ}\left\{\left(\frac{s_{LJ}}{r}\right)^{12} - \left(\frac{s_{LJ}}{r}\right)^{6}\right\}
\]  

(1)

However, it is practically hard to properly set the interaction between Au and Si atoms. Therefore, we consult experimental results which is using atomic force microscopy (AFM). In the experiment, AFM probe made of silicon is interacted with Au cluster-assembled structure (produced by sintering of 8nm Au clusters). We obtain adhesive force between the AFM probe and that gold surface by the method of indentation test and its force curve. The largest force occurring there is averaged over surface atoms, and the maximum force and energy (cohesive energy) at contact is obtained. As a result, the value of LJ parameter corresponding cohesive energy is \( e_{LJ,\text{Si-Au}(1)} = 1.32 \times 10^{-20} \) J, which is much smaller than that averaged between Au-Au and Si-Si interactions by conventional Lorentz-Berthelot law. Nevertheless, since the way of calculating parameter for Si-Au includes ambiguity, we also adopt other two LJ parameter values for MD simulations: \( e_{LJ,\text{Si-Au}(2)} = 0.85 \times 10^{-20} \) J and \( e_{LJ,\text{Si-Au}(3)} = 0.40 \times 10^{-20} \) J. The LJ potential curves used in the simulation are summarized in Fig.2.

![Fig. 2 Potential energy function for Si-Au (3-kinds) and Si-Si](image)

2.3. Analysis of strain, stress and crystalline structure

A structure of atomic cluster deforms by applied external load. The change of shape is effectively captured by strain analysis. Strain of the whole atomic cluster can be evaluated as follows. First, one can estimate six components of Green-Lagrange strain on the Cartesian coordinates \((x, y, z)\). For example, normal \( x \) component and shear \( xy \) or \( yx \) component of strain are given by,

\[
\varepsilon_x = \frac{l_x - l_x^0}{l_x^0}, \quad \varepsilon_{xy} = \varepsilon_{yx} = \frac{1}{2} \left( \frac{l_y - l_y^0}{l_y^0} + \frac{l_x - l_x^0}{l_x^0} \right),
\]  

(2)
where \( l_x, l_y \) and \( l_0^x, l_0^y \) are current and initial lengths of the cluster in corresponding direction, respectively. These lengths are measured by distance between positions of outermost atoms along the corresponding direction. Six components \((\varepsilon_x, \varepsilon_y, \varepsilon_z, \varepsilon_{xy}, \varepsilon_{yz}, \varepsilon_{zx})\) are recognized as strain tensor matrix and, therefore, can be diagonalized into three principal strains \( \varepsilon_1, \varepsilon_2, \varepsilon_3 \). Three principal strains represent major stretch or compression axes and are utilized for deriving just shape change excluding rotation.

Stress of the cluster is obtained by averaging atomic stress which is calculated immediately from interatomic potential\(^{(10)}\). Type of crystalline structure is identified by conventional method of common neighbor analysis (CNA)\(^{(11)}\). By using topological connection among neighbor atoms as well as coordination number, this method has been developed to categorize four kinds of crystalline structure, that is, (1) f.c.c. structure, (2) h.c.p. structure, (3) surface, and (4) other defect structure. Atoms in the third category, "surface", is identified as low coordination number less than 12. If these atoms appear inside a condensed body, they are guessed amorphous or liquid structure. Since these atoms are typically found in surface, they are called "surface" in our CNA, just for convenience. In the present paper, in seeing atomic configuration, we are adding atomic coloration of gray, red, blue, and brown, for four categories in order listed above (1∼4).

3. Results and Discussion

3.1. Characteristics of deformation

In order to comprehend the effect of temperature, we begin with comparison between \( T=0 \) K and 300 K cases. Figures 3 and 4 show evolution of atomic configurations during compressive loading and subsequent unloading, at \( T=0 \) K and 300 K, respectively. It is well observed that the total deformation in 300 K is larger than that in 0 K. In both temperatures, the cluster undergoes a flattened shape. Besides, only in \( T=300 \) K, adsorption of the cluster to one of Si plates is observed. This adsorption is understood as "physisorption" (physical adsorption) which would be accelerated by thermal fluctuation.

A lot of lattice defects inside the deformed cluster are confirmed by using CNA technique. The figures show cross sections which is parallel to \( xy \) plane and crosses at the center of the cluster (i.e. the plane is \( z=0 \)). The basic crystalline structure of the cluster is composed of two layers, where f.c.c. crystals (gray) are surrounded by surface atoms (blue). In contacting Si plates, region of surface atoms propagate into inside the body. However, after unloaded, those new surface atoms changes back to initial f.c.c. state. In 300 K, at the end of unloading, it is recognized that plane regions of h.c.p. atoms (stacking fault planes) are detected clearly. This behavior is quite the same as deformation twin observed in MD simulation of aluminum cluster-assembled structure\(^{(12)}\). Since, stacking fault energy of gold is very small and width of extended dislocation may be remarkably longer than other ductile metals, it makes sense that planes of stacking fault penetrate the cluster body. Stacking faults do not transform into perfect dislocation but are stabilized by themselves, especially for the small-sized cluster like this.

3.2. Characteristics in stress-strain relation

Next, we examine change of shape and stress state in the cluster. They are carried out by using strain measurement and averaged atomic stress as described in previous section. Figures 5(a) and (b) show stress-strain (SS) curves for \( T=0 \) K and 300 K, respectively. Normal stress and strain components in \( y \) direction are inspected. From the time of contact to the Si substrate, the SS curve shows linear relation, meaning elastic response, and then reaches yield point. Yield stress is about 2 GPa in \( T=300 \) K, whereas it arises to 20 GPa in \( T=0 \) K. Yield strain in \( T=300 \) K exceeds 30%, which is considerably larger than that of 0 K. This behavior depending on temperature means that the higher the temperature is, the more deformable the cluster body is. In \( T=0 \) K case, the SS curve looks like a typical load-displacement curve
Fig. 3 Transition of atomic configuration in $T=0$ K; time progress and indentation length are indicated in each pictures; the cross section at $z=0$ is shown.

Fig. 4 Transition of atomic configuration in $T=300$ K; time progress and indentation length are indicated in each pictures; the cross section at $z=0$ is shown.
obtained in nano-indentation experiment. Even at the end of the simulation, both curves do not return to the initial condition (the origin) and show hysteresis besides. Though it seems like plastic deformation, one can also recognize large recovery in strain.

It is surprising that the recovery strain of the cluster is remarkably large compared with bulk metal gold (usually, ~0.2% or less). The recovery strain $\varepsilon_{rc}^{ij}$ can be defined as the difference of nominal strains between the most squeezed shape (e.g., Fig.3(2)) and the final relaxed shape (e.g., Fig.3(6)). With our strain definition, Eq.(2), the expression of $\varepsilon_{rc}^{y}$ in $y$ direction would be:

$$
\varepsilon_{rc}^{y} = \varepsilon_{f}^{y} - \varepsilon_{m}^{y} = \left( \frac{l_{f}^{y} - l_{0}^{y}}{l_{0}^{y}} - \frac{l_{m}^{y}}{l_{0}^{y}} \right) = \frac{l_{f}^{y} - l_{m}^{y}}{l_{0}^{y}} (> 0) ,
$$

where superscript $f$ and $m$ mean the final state and the most squeezed state, respectively. The calculated values of $\varepsilon_{rc}^{y}$ are 8.05% and 6.37% for $T=0$ K and 300 K, respectively. Note that, in unloading of 300 K case, as denoted in Fig.5(b), the SS curve enters the tensile stress region. This is understood that the cluster is being stretched by Si plates in that period. This effect is depending on interaction strength between Au and Si atoms. This issue will be discussed in later section.

Fig. 5 Stress-strain relation of the Au cluster in compressive loading and subsequent unloading processes (in normal $y$ direction): note that stress range used in two graphs are very different.

Transition of principal strains shows unique behavior. Figure 6 shows the time transition of principal strains in loading and unloading. The largest in absolute value is $\varepsilon_{1}$, which corresponds to compressing direction. The second largest is $\varepsilon_{2}$, which is perpendicular to $\varepsilon_{1}$ and is parallel to the Si plate. However, it is found that another principal value, $\varepsilon_{3}$, shows always zero. This means the fact that the cluster exhibits not a triaxial deformation but a biaxial one. The reason for biaxial deformation is guessed as follows. Generally, the slip deformation is dominant in the cluster. Therefore, in a small cluster such with 4 nm or less diameter, slip planes and directions are not organized with crossing behavior since it is small, but then they tend to be assembled to a single orientation (illustration is drawn in Fig.6 marginally).

3.3. Details of crystalline structural change

Here, we quantify crystalline structural change in the cluster. The CNA analysis described above is useful to comprehend atom-by-atom transition of crystalline structure. Figure 7 shows time transition of the number of atoms in four categories. The vertical axis of the figures shows the ratio, which is defined as a fraction of the number of atoms in that category to the number of all atoms in the cluster. By being compressed by substrates, f.c.c. atoms decreases and surface atoms increases. Once unloading starts, f.c.c. structures recover and surface atoms diminish. Since h.c.p. atoms, i.e. stacking faults, are limited to area of slip plane, their ratio is relatively small. In unloading, growth of h.c.p. atoms is not recognized in $T=0$ K, whereas
in 300 K the graph shows finite increase of h.c.p. atoms up to 10%. In higher temperature, atoms are moving more diffusively and therefore produce stacking faults promptly with more ease.

The surface atoms temporarily increases up to the most squeezed strain (indicated by vertical arrow in the graph). These atoms that detected as ”surface” but found inside cluster are recognized as amorphous structure. Since the amorphous structure in 300 K is never stable, they disappear during unloading process. However, in much higher temperature such as near $T_m$, the amorphous atoms become relatively stable and are able to stay inside the cluster during unloading.

3.4. Dependence on temperature

Figure 8 shows the temperature dependence of recovery strain in $y$ (loading) direction ($\varepsilon_{rec}^y$). In low temperature ($T = 0 \sim 400$ K), $\varepsilon_{rec}^y$ is around 5~10%. Above $T=400$ K, $\varepsilon_{rec}^y$ increase considerably. In particular, near the melting temperature $T_m$ for the cluster (shown in Table 2), the increase is drastic. In this case, if $e_{LJ}$ corresponding adhesive strength is strong, the cluster is stretched like a bridge between Si plates in unloading process and results in large tensile strain. Generally speaking, it is understood that, since above $T_m$ the structure becomes amorphous or almost liquid-like, ability to recover shape is governed by the mechanism of minimizing surface energy, namely, surface area. But, to the contrary in lower temperature, recovering shape is governed not by such surface mechanism but by reconstruction of atoms through internal slip.

3.5. Dependence on Au-Si interaction

In unloading process, a squeezed and smashed cluster is pulled back by two Si plates and there arises tensile stress, as shown in Fig.5. Since interaction parameter $e_{LJ}$ for LJ potential of Au and Si atoms determines degree of pulling force, we check dependence on that parameter. Figure 9 compares SS curves for different $e_{LJ}$ in 300K. It is true that both temperature and the LJ parameter $e_{LJ}$ influence SS curves. We do not gain general understanding of SS curve, but we are able to comment on it as follows. The behavior of loading process is almost the same for three parameters, whereas in unloading tensile stress reduces with smaller $e_{LJ}$ which induces smaller attractive force. This fact means that recovery strain in the cluster is caused possibly by two factors. One is attractive interaction between Au and Si atoms. Another is self-recovery process in shape induced by internal unstable crystalline structures. Looking at Fig.8, reducing $e_{LJ}$ results in small recovery strain. However, with the smallest $e_{LJ}$ ($0.40 \times 10^{-20}$ J) where attractive force is almost negligible, recovery strain is there. Thus, it is still reasonable to think that the cluster itself has an ability to recover its shape from largely...
Fig. 7 Transition of crystalline structures: for $T = 0$ K and 300 K, with $e_{LJ} = 1.32 \times 10^{-20}$ J.

Fig. 8 Dependence of recovery strain $\varepsilon_{rec}$ on temperature (comparison among $e_{LJ}$s).
strained state toward original structure. It is concluded that the small atomic cluster possesses an ability to recover its shape with extraordinarily large recovery strain in the super-elastic regime.

![Figure 9: Comparison of stress-strain curve for various LJ parameters, $\varepsilon_{LJ}$, in 300 K](image)

4. Conclusion

We performed molecular dynamics simulation for investigating extraordinary elastic response of gold (Au) atomic cluster. It is concluded that the small gold (Au) atomic cluster shows unique behavior in compression and subsequent unloading. It will lead to more general super-elastic or rebounding behavior of nano-sized atomic clusters. This paper also describes some methodologies with regard to modeling and analysis for mechanical properties. Following results are obtained.

1. In the temperature range from 0 to 400 K, recovery strain is around 5%–10%. It is considerably larger than ordinary value known in bulk gold.
2. A cluster with 4 nm diameter deforms by slip motion and results in stacking faults appearing across cluster’s body. Since these slips occur in the same direction, deformation of whole body becomes not triaxial but biaxial. This fact can be verified in the analysis of principal strain of which we formulate definition.
3. In high temperature (above melting temperature of the cluster), crystalline structure tends to be amorphous and shows much more recovery strain. This is because the shape change is carried out not only by slip deformation mechanism but by stronger mechanism of minimizing surface energy or area.
4. When silicon plates separate each other in unloading process, atomic cluster feels attractive force and resulted in tensile stress. Reducing interaction strength between Au and Si atoms, tensile stress diminishes. Nevertheless, large shape recovery occurs even if the attractive force mostly vanishes. It is concluded that the small atomic cluster has an ability to recover the original shape, which is recognized as extraordinary elasticity, namely, super-elasticity.

We do not report size effect of the cluster. Larger cluster is supposed to exhibit more complicated deformation. We believe that our research establishes the basis for further research as for super-elastic behavior appearing in atomic clusters.

Acknowledgements

This research was supported by JSPS KAKENHI(21560103) (2009), HRC Kansai University, and the Kansai University Grant-in-Aid for progress of research in graduate course, 2008.
References


