

# Melting of Mackay icosahedral gold clusters from molecular dynamics simulations

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Molecular dynamics simulations show that liquid gold clusters with about 500 - 5000 atoms crystalize to a Mackay icosahedron upon a certain cooling procedure. Detailed surface analysis shows that the facets of the Mackay icosahedral gold clusters do not premelt, but that the surface softens below the bulk melting temperature. We owe this softening to the increasing mobility of vertex and edge atoms with temperature, which leads to inter- and intra-layer diffusion, and a shrinkage of the average facet size, so that the average shape of the cluster is nearly spherical at melting.

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## I. INTRODUCTION

Nanocrystals have quite different physical properties from their corresponding bulk materials mainly because of their large surface-to-volume ratio. Among noble metals, gold nanoparticles have already shown their promise for a wide range of applications<sup>1-4</sup>. Thus knowledge of the structure and stability of gold nanocrystals are essential for future applications.

While bulk gold has an fcc crystal structure, the competition between bulk and surface energies in nanometer sized gold crystallites can result in several different competing structures<sup>6,7</sup>. Depending on cluster size and external conditions, transitions between these structures have been observed<sup>7,8</sup>. One such structure which has been observed both in simulations<sup>9,10</sup> and in experiment<sup>11,12</sup>, is the "Mackay icosahedron"<sup>13,14</sup>, consisting of 20 slightly distorted fcc tetrahedra, with four {111} facets each, meeting at the center to form an icosahedral shaped cluster. The internal facets of the tetrahedra meet at strain inducing twin grain boundaries with hcp structure, leaving the cluster with 20 external {111} facets. Theoretical models<sup>15-17</sup> have predicted different limits for the stability of such icosahedral clusters, and it is unclear whether their formation is an equilibrium or rather a kinetic process<sup>11,16-20</sup>. Nevertheless, it is natural to suppose that formation of this structure is related to the very high stability of the {111} external surfaces. Simulations<sup>21</sup> and experiments<sup>22</sup> on bulk slab-like geometries with exposed {111} surfaces have shown that, unlike the {100} and {110} surfaces which melt below the bulk melting temperature  $T_m$ , the {111} surface is a nonmelting surface without roughening, wetting, or melting up to the bulk melting temperature  $T_m$ , and can in fact lead to superheating of the solid<sup>23</sup>. In light of this observation

it is interesting to consider how the high stability of the {111} facets affects the melting and equilibrium shape of such icosahedral clusters.

In this paper, we will show, by molecular dynamics (MD) simulations, that liquid gold clusters with about 500 - 5000 atoms crystalize to a Mackay icosahedron (Ih) upon a certain cooling procedure. With these obtained Ih gold clusters, we pay particular attention to the behavior of the surface atoms and the equilibrium shape when increasing temperature towards  $T_m$ . Unlike earlier results on smaller cuboctahedral clusters<sup>32</sup>, which include non {111} facets that premelt below  $T_m$ , we find no surface premelting or roughening of the {111} facets of our Ih clusters. Nevertheless, we find that there is a considerable softening of the cluster surface roughly  $\sim 200\text{K}$  below  $T_m$  due to the motion of atoms along the vertices and edges of the cluster. In this region we find both intra-layer and inter-layer diffusion of atoms, which increases considerably as  $T_m$  is approached. The equilibrium shape progresses from fully faceted, to faceted with rounded edges, to nearly spherical just below  $T_m$ . Throughout this region, the interior atoms of the cluster remain essentially perfectly ordered, until  $T_m$  is reached. \*\*\*Nevertheless, we find no evidence of a separated faceting transition from the first order melting transition of the bulk.\*\*\*

## II. METHODS

### A. Simulation model and methods

On today's computers *ab initio* simulation techniques providing an accurate description of interaction energies can be used to simulate systems consisting of up to hundreds of atoms<sup>7</sup>. However, they are too

time demanding in computations to allow long time simulations. Using less accurate but computationally less expensive model potentials, such as the embedded atom method<sup>7</sup>, the Murrell-Mottram potential<sup>7</sup>, the Lennard-Jones potential<sup>7</sup>, the Morse potential<sup>7</sup>, the many-body Gupta potential<sup>7</sup>, or the many-body “glue” potential<sup>7</sup>, one can extend the size of simulated gold nanoclusters to more than ten thousand atoms. In this study, we have chosen the many-body “glue” potential because it was found to yield an accurate description of the bulk, defect and surface properties of gold<sup>7</sup>. In the “glue” model, the potential energy of a system of  $N$  atoms consists of a sum of pair potentials  $\phi$  and a many-body “glue” energy  $U$ :

$$V = \frac{1}{2} \sum_i \sum_{j \neq i} \phi(r_{ij}) + \sum_i U(n_i). \quad (1)$$

Here the sums run over all particles,  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  is the interatomic distance between atoms  $i$  and  $j$ , and  $\phi(r)$  is the pair interaction energy with a cutoff of 3.7Å. The many-body “glue” energy  $U(n_i)$  depends on the coordination numbers  $n_i$  defined for all atoms,

$$n_i = \sum_j \rho(r_{ij}), \quad (2)$$

where  $\rho(r)$  is a short-ranged monotonically decreasing function of the interatomic distance  $r$  with a cutoff of 3.9Å. The equations of motion are integrated with the velocity Verlet algorithm<sup>7</sup> with a time step of 4.3fs. This time interval is comparably large to save computational time, while keeping the numeric error of energy caused by finite time step in  $10^{-5}$ eV per atom.

Because the many-body “glue” potential has cutoffs, a cell index method can be used to reduce the computational time<sup>7</sup>. In this method, the simulation box is divided into cubic cells with side lengths larger than the cutoff distance (3.9Å for gold glue model). When calculating energies and forces one considers only interactions between atoms within the same cell and the neighboring 26 cells. This approach reduces the required computation time from order  $N^2$  to order  $N$ . On a PC equipped with a 1.5GHz AMD Athlon CPU and 1GB of memory, 25,000 steps can be carried out per CPU-hour for a system of 2,624 atoms propagating the system for about 100ps.

The Andersen thermostat<sup>26</sup> is a MD method which can mimic a system coupled to a heat bath with constant temperature. At each step a particle is chosen randomly and assigned with a new velocity sampled from the Boltzmann distribution of a given temperature. The Andersen thermostat samples both configuration and momentum spaces correctly, so that the instantaneous kinetic temperature fluctuates, as real systems do. However, with the Andersen thermostat, a system does not conserve its linear and angular momenta so that it translates and rotates, hence dynamical properties like diffusion coefficients can not be directly obtained.

A more naive approach to keep a system at constant temperature is to crudely rescale the velocities of all particles to the given temperature at each step. This scheme gives unphysical results because the instantaneous kinetic temperature does not fluctuate. Nevertheless, it correctly samples configuration space, so that it is a more convenient way than the Andersen thermostat as long as our study does not measure quantities in momentum space. We imprecisely but evidently call this method constant temperature MD.

In our simulations the gold clusters were cooled down by the Andersen thermostat, and then heated up and equilibrated by constant temperature MD, when the dynamical properties were tracked.

## B. Quantifying structure by bond orientational order parameters

Both the bulk and the surface structures of gold nanoclusters were quantified by calculating the bond orientational order parameters<sup>7</sup>. A bond is defined as the vector joining a pair of neighboring atoms. (Through our paper, for a given gold atom, its nearest neighboring atoms are defined as those atoms who have an interatomic distance of less than a certain cutoff radius of 3.8Å to the given atom, which is the minimal value between the first and the second peaks of the pair correlation function). The general idea of bond order parameters is to capture the symmetry of bond orientations regardless of the bond lengths. The local order parameters associated with a bond  $\mathbf{r}$  are the set of numbers

$$Q_{lm}(\mathbf{r}) \equiv Y_{lm}(\theta(\mathbf{r}), \phi(\mathbf{r})), \quad (3)$$

where  $\theta(\mathbf{r})$  and  $\phi(\mathbf{r})$  are the polar and azimuthal angles of the bond with respect to an arbitrary but fixed reference frame, and  $Y_{lm}(\theta(\mathbf{r}), \phi(\mathbf{r}))$  are the usual spherical harmonics. Only even- $l$  spherical harmonics are considered so that they are invariant under inversion. Global bond order parameters can then be calculated by averaging  $Q_{lm}(\mathbf{r})$  over all bonds:

$$\bar{Q}_{lm} \equiv \frac{1}{N_b} \sum_{\text{bonds}} Q_{lm}(\mathbf{r}), \quad (4)$$

where  $N_b$  is the number of bonds. To make the order parameters invariant with respect to rotations of the reference frame, the second-order invariants are defined as

$$Q_l \equiv \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{Q}_{lm}|^2}, \quad (5)$$

and the third-order invariants are defined as

$$W_l \equiv \sum_{\substack{m_1, m_2, m_3 \\ m_1 + m_2 + m_3 = 0}} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \bar{Q}_{lm_1} \bar{Q}_{lm_2} \bar{Q}_{lm_3}, \quad (6)$$

where the coefficients  $(\dots)$  are the Wigner  $3j$  symbols<sup>7</sup>. Furthermore, a normalized quantity

$$\hat{W}_l \equiv \frac{W_l}{\left(\sum_m |Q_{lm}|^2\right)^{3/2}} \quad (7)$$

independent of  $\{Q_{lm}\}$  for a given  $l$  is more quantitative to measure the symmetry of a cluster.

We used the four bond order parameters  $Q_4$ ,  $Q_6$ ,  $\hat{W}_4$  and  $\hat{W}_6$  to identify structures accurately. Based on our calculations, the values of these bond order parameters for 13-atom fcc, hcp, icosahedral, and liquid local structures along with three primary fcc surfaces  $\{100\}$ ,  $\{110\}$  and  $\{111\}$  are listed in Tab. I.

The bond orientational order parameters, averaged over all bonds, can be used to monitor global structural changes. Surface structures of nanomaterials, however, are often quite different from bulk structures. We therefore calculated bond order parameters for the internal atoms and the surface atoms separately. Surface atoms were discriminated accurately by using a newly developed ‘‘cone’’ algorithm, as described below. Because the bulk order parameters measure three dimensional structures, while the surface order parameters include only bonds within a two dimensional surface, the values of surface and bulk order parameters can be quite different even for a uniform structure. It is also noticeable that above the cluster melting temperature, the bond order parameters take finite values instead of the value of zero that one would expect in a disordered liquid. This is a finite size effect, and we find that, in the liquid, the absolute values of the parameters decrease as the cluster size increases.

### C. Geometrical analysis of the surface

#### 1. Cone algorithm

A ‘‘cone’’ algorithm has been developed to discriminate surface particles accurately according to their geometrical positions. For a given particle, we define an associated *cone region* as the region inside a cone of side length  $a$  and angle  $\theta$ , whose vertex resides on the particle. A *hollow cone* is a cone region with no other particles inside it. We take a particle to be on the surface if at least one associated hollow cone can be found.

The cone algorithm is intrinsically consistent with the general definition of surface particles. It can pick up all of the particles on a convex surface. For the particles on a concave surface, the precision of identifying a surface atom relies on the choice of the parameters  $a$  and  $\theta$  (Fig. 1). By visual examination of our generated configurations, we found that the two parameters  $a = 5.0\text{\AA}$  and  $\theta = \frac{\pi}{3}$  gave good results for our clusters.

The cell index method mentioned above, and other numerical optimization approaches, have improved the computational speed of the implementation of this algorithm. For a gold cluster with 5082 atoms, we need

only one and a half seconds CPU to determine the surface atoms. The cone algorithm can also be applied recursively to divide particles into surface and sub-surface layers to allow interlayer analysis. Fig. 4 shows a planar slice cut through an instantaneous configuration of a gold cluster with 2624 atoms at  $T = 200\text{K}$  (Ih) and  $T = 1200\text{K}$  (liquid) respectively. From this figure we can see that the cone algorithm works well on both solid and liquid configurations.

#### 2. Roughness and curvatures

In order to quantify the surface morphology of clusters, we compute the roughness, the bond curvature and the local curvatures associated with each particle as defined below.

For each particle on the surface of the cluster we define the tangent plane to the cluster at that point as follows. We consider the collection of particles determined by the particle of interest and all its nearest neighbor particles which are also on the surface. We require the tangent plane to pass through the center of mass of these particles, and we determine its orientation by minimizing the root mean square distance of the particles to the plane. We solve for this plane as follows. If  $\mathbf{n} \equiv (n_x, n_y, n_z)$  is the (unsolved) normal vector of the tangent plane,  $\mathbf{r}_i \equiv (x_i, y_i, z_i)$ ,  $i = 1 \dots N_s$  is the coordinate of the  $i$ th particle,  $N_s$  is the number of particles, and  $\mathbf{r}_c \equiv (x_c, y_c, z_c)$  is the coordinate of the center of mass, then the distance from the  $i$ th particle to the tangent plane is

$$d_i = \mathbf{n} \cdot (\mathbf{r}_i - \mathbf{r}_c). \quad (8)$$

The problem of finding the normal vector of the tangent plane (and thus the plane itself) is equal to the problem of minimizing the *discrete differential roughness*  $H$  of a local geometry:

$$H = \sqrt{\frac{F}{N}}, \quad (9)$$

where  $F \equiv \sum_i d_i^2$ . The minimal value of  $F$  is found by applying an undetermined Lagrange multiplier  $\lambda$ :

$$\frac{\delta}{\delta \mathbf{n}} [F - \lambda (\mathbf{n}^2 - 1)] = 0. \quad (10)$$

Eq. (10) leads to the symmetric eigenvalue problem:

$$\begin{pmatrix} XX - \lambda & XY & XZ \\ XY & YY - \lambda & YZ \\ XZ & YZ & ZZ - \lambda \end{pmatrix} \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = 0, \quad (11)$$

where  $XY = \sum_i (x_i - x_c)(y_i - y_c)$ , and other quantities are computed similarly. The minimal solution of  $\lambda$  among three possible eigenvalues is the minimizing value of  $F$ , and its associating eigenvector  $(n_x, n_y, n_z)$  is the normal

vector of the tangent plane  $\mathbf{n}$ . The roughness  $H$  is then obtained from Eq. (9).

One statistical way to quantify the morphology of the entire surface is to measure the *bond curvature* for all bonds connecting two neighboring surface particles. Once the optimized tangent planes have been found for all particles, a bond curvature  $c_b$  is given by the normal vectors  $\mathbf{n}_1$  and  $\mathbf{n}_2$  of the planes associated with two neighboring particles  $\mathbf{r}_1$  and  $\mathbf{r}_2$ :

$$c_b \equiv \frac{1}{r} = \frac{2\sin(\theta/2)}{L}, \quad (12)$$

where  $\theta = \text{acos}(\mathbf{n}_1 \cdot \mathbf{n}_2)$  is the angle between the two normal vectors, and  $L = |\mathbf{r}_1 - \mathbf{r}_2|$  is the distance between the two particles (Fig. 2).  $r$  in the above (see Fig. 2) is the radius of the sphere that fits through the two neighboring surface points with the same tangent planes.

Alternatively, we can compute the curvature of the surface at each particle on the surface as follows. Since the neighboring geometry is roughly a 3D surface, we fit the geometry with a paraboloid surface. The *maximal local curvature* and the *minimal local curvature* are just given by the two principle curvatures of the fitted paraboloid. The scheme of this idea is shown in Fig. 3.

To fit the paraboloid at particle  $\mathbf{r}_0$ , we take the normal vector to the surface  $\mathbf{n}$  at  $\mathbf{r}_0$ , as computed above, and define this to be the local  $z$ -axis. We place the origin at  $\mathbf{r}_0$  and then choose  $x$  and  $y$  axes in the tangent plane. We can now define the coordinates  $(x_i, y_i, z_i)$  of neighboring particle  $\mathbf{r}_i$ , in the coordinate system. We then choose a fitting paraboloid function:

$$f(x, y) = a_{xx}x^2 + 2a_{xy}xy + a_{yy}y^2, \quad (13)$$

and minimize

$$S = \sum_i (z_i - f(x_i, y_i))^2, \quad (14)$$

with respect to  $a_{xx}$ ,  $a_{xy}$ , and  $a_{yy}$ . This leads to the following set of linear equations

$$\begin{pmatrix} \sum_i x_i^4 & \sum_i x_i^3 y_i & \sum_i x_i^2 y_i^2 \\ \sum_i x_i^3 y_i & \sum_i x_i^2 y_i^2 & \sum_i x_i y_i^3 \\ \sum_i x_i^2 y_i^2 & \sum_i x_i y_i^3 & \sum_i y_i^4 \end{pmatrix} \begin{pmatrix} a_{xx} \\ 2a_{xy} \\ a_{yy} \end{pmatrix} = \begin{pmatrix} \sum_i x_i^2 z_i \\ \sum_i x_i y_i z_i \\ \sum_i y_i^2 z_i \end{pmatrix} \quad (15)$$

Solving Eq. (15) for  $a_{xx}$ ,  $a_{xy}$ ,  $a_{yy}$ , we diagonalize the symmetric matrix of  $((a_{xx}a_{xy}), (a_{xy}a_{yy}))$  to obtain the two principle axes and the corresponding eigenvalues  $\lambda_1$  and  $\lambda_2$ . The local curvatures are then given by  $\kappa_{1,2} = \frac{1}{2}\lambda_{1,2}$ . It turns out that the maximal local curvature is very helpful to coloring the surface atoms in order to visualize the vertex, edge and facet atoms.

To test our above methods, we have computed the bond curvature of an ideal Ih gold cluster with a magic number of atoms equal to 2868 (see Fig. 7c). In Fig. 5 (top row) we show the resulting histograms of bond curvatures, maximal local curvature, and roughness. All three histograms have three  $\delta$  functions corresponding to

the facets, the edges and the vertices, with the exception of the bond curvature distribution, where two peaks exist as the vertex region. Those two peaks correspond to the bond curvatures between the vertex atoms and the edge atoms, and the vertex atoms and the facet atoms respectively. We also test our method for a liquid gold cluster with 2624 atoms at  $T = 1200\text{K}$  (see Fig. 6c). We show our results in Fig. 5 (bottom row). Each histogram has just one peak of finite width. The peaks of the bond curvature and the maximal local curvature are both centered at  $1/R = 0.047\text{\AA}^{-1}$ , with  $R = 21.5\text{\AA}$  the radius of the spherical liquid drop.

### 3. Average equilibrium shape

At low temperature, the atoms in the gold cluster remain at well defined equilibrium positions and only oscillate thermally around the vicinity of these equilibrium positions. The shape of the cluster is thus easily determined from an instantaneous configuration. At high temperature, however, atoms become more mobile and the macroscopic shape of the cluster fluctuates dramatically from configuration to configuration. In this case it becomes necessary to average over many fluctuating configurations to define the average cluster shape. Since our constant temperature MD conserves both linear and angular momentum, the configurational shape changes we average over represent fluctuations of the surface atoms rather than trivial shifts or rotations of the cluster as a whole.

In Fig. 6a we show four arbitrary instantaneous configurations of liquid gold nanoclusters with 2624 atoms at  $T = 1200\text{K}$ . By using the cone algorithm, we extracted the surface atom positions from totally 1000 configurations sampled from 43ns equilibrium simulation. After we overlapped them together and projected them to an arbitrary plane, we got a perfect circular distribution shown in Fig. 6b. This suggests that the liquid surface probably vibrates around a spherical equilibrium shape.

In order to get the average equilibrium shape, we divided the  $4\pi$  sphere centered at the center of mass into cone cells with almost equal solid angles given by the best covering spherical codes with icosahedral symmetry developed by Hardin *et al.*<sup>31</sup>. The surface atom positions in each cell were then averaged to get the average equilibrium shape. The obtained average shape of the liquid cluster is indeed a perfect sphere as shown in Fig. 6c. Different number of cells results in different resolution, and we always choose that closest to the number of surface atoms in one configuration.

### D. Atom mobility analysis

With enough kinetic energy, atoms can hop around their crystal sites and even travel across the whole cluster. The mean squared displacement (MSD) is a conve-

nient way to measure the average ability of movement for a group of atoms. The MSD is defined as

$$MSD(\Delta t) = \frac{1}{MN} \sum_{j=1}^M \sum_{i=1}^N (\mathbf{r}_i(t_j + \Delta t) - \mathbf{r}_i(t_j))^2, \quad (16)$$

where  $\mathbf{r}_i$ ,  $i = 1 \dots N$  is the position of atoms,  $N$  is the number of atoms,  $\Delta t$  is the time interval with  $t_j = t_{j-1} + \Delta t$ ,  $M$  is the number of time intervals, which are chosen to be independent from each other. For an infinite three dimensional bulk system, we expect that  $MSD = 6Dt$  as  $t \rightarrow \infty$ . In a finite cluster however, the MSD will eventually saturate on a length scale comparable to the cluster size. We therefore determine the diffusion coefficient  $D$  by fitting  $MSD(\Delta t)$  to the early linear part before saturation takes place.

A visual way to quantify the magnitude of an atom's displacement is the *ellipsoid movement representation*. For each atom in  $N$  successive configurations, the ellipsoid mean squared displacement is given by a  $3 \times 3$  matrix  $C \equiv \{C_{\mu\nu}, \mu, \nu = x, y, z\}$ , and

$$C_{\mu\nu} = \frac{1}{N} \sum_{i=1}^N (r_{i\mu} - \langle r_\mu \rangle)(r_{i\nu} - \langle r_\nu \rangle), \quad (17)$$

where  $\mu, \nu = x, y, z$ ,  $r_{i\mu}$  is the coordinate in one configuration, and  $\langle r_\mu \rangle$  is the average coordinate over all  $N$  configurations. The probability of the atom in position  $\mathbf{r}$  is  $P(\mathbf{r}) \sim \exp(-\frac{1}{2}(\mathbf{r} - \langle \mathbf{r} \rangle)C^{-1}(\mathbf{r} - \langle \mathbf{r} \rangle))$ , and the function of the ellipsoid surface is

$$(\mathbf{r} - \langle \mathbf{r} \rangle)C^{-1}(\mathbf{r} - \langle \mathbf{r} \rangle) = 1. \quad (18)$$

In practice we take the eigenvectors of  $C$  and the square root of their corresponding eigenvalues to define the axes and principal radii of an ellipsoid to allow us drawing the ellipsoids in the visualization software.

### III. RESULTS

Gold clusters with more than 5000 atoms require too much computational time to allow long time simulation and complete detailed analysis. On the other hand, those with too few atoms have too small facets and too soft surface to allow us distinguish the facets behavior from vertices and edges clearly. So we simulated several sizes between 500 and 5000 atoms, and concentrated on the moderate size of 2624 atoms.

#### A. Mackay Icosahedra

We started with a liquid gold cluster with 2624 atoms at 1500K, and equilibrated it at 1000K for  $5 \times 10^6$  steps (21.5ns) by using the Andersen thermostat. We then cooled down the cluster to 200K with intervals of 100K. At each temperature the system is also equilibrated for

$5 \times 10^6$  steps (21.5ns). With this cooling method we got a Mackay icosahedron<sup>13</sup> with a missing central atom. The energetics of such vacancies at the center of icosahedral clusters were first considered by Boyer and Broughton<sup>27</sup> for Lennard-Jones clusters and later by Mottet *et al.*<sup>28</sup> for Cu, Ag, and Au particles. Above a certain material dependent critical size the central vacancy lowers the energy of the cluster by partially releasing the strain caused by the mismatch of the tetrahedral units. Mottet *et al.* concluded that for gold particles the introduction of the central point defect does not lower the energy enough to make the icosahedron competitive with crystallographic octahedra and Wulff polyhedra. This conclusion is, however, solely based on energy calculations neglecting entropic contributions to the free energy. Our simulations indicate that such a constitutional vacancy, possibly jointly with thermal effects, sufficiently stabilizes icosahedral clusters of thousands of atoms making them the predominant species.

The well known Wulff construction<sup>15</sup> can obtain the equilibrium morphology of a single crystal by minimizing its surface free energy while imposing the constraint of constant volume. This method is based on continuum concepts and is therefore appropriate only for large particles. Small gold particles, for which corner and edge energies become important, can display multiply twinned decahedral and icosahedral shapes with crystal structures differing from the fcc arrangement of the bulk material. These structures can be thought as consisting of fcc tetrahedra joining at so called twin boundaries. An icosahedron, for instance, consists of 20 distorted fcc tetrahedra, with four fcc {111} facets each, meeting at the center of the crystallite. The tetrahedra do not match perfectly introducing a strain at the twin boundaries. In the small size regime, the energetically unfavorable strain is compensated by the low surface energy of the twenty exposed fcc {111} facets. Using a continuum approach to take into account the strain energy and the twin boundary energy, Ino predicted that icosahedral clusters are stable up to sizes of 40,000 atoms<sup>16</sup>. For larger clusters, structures with fcc arrangement and various shapes are predicted to have a lower energy than icosahedral particles. Similar stability limits for icosahedral gold particles were predicted by Marks using a modified Wulff construction<sup>11,20</sup>. More recent atomistic calculations indicate that icosahedral gold nanoclusters are energetically competitive only in a very small size range of tens of atoms<sup>17-19</sup> (entropic effects were neglected in these studies). However, in molecular dynamics simulation of freezing gold nanoparticles Chushak and Bartell<sup>9</sup> observed icosahedral particles of up to almost 4000 atoms. Furthermore, Cleveland *et al.*<sup>7</sup> found that upon heating gold clusters consisting of hundreds of atoms transform from the energetically optimal truncated-octahedral shape with fcc structure to icosahedral structures. Thus, icosahedral particles might indeed be the thermodynamically most stable structure under appropriate conditions rather than just originating from kinetic factors such as the growth mechanism. Al-

though we have no guarantee that we have found the true equilibrium shape, the comparably long simulation time of 43ns at each temperature reduces our suspicion that the clusters might be trapped in an out-of-equilibrium structure.

Because 2624 is not one of the magic numbers of Ih structure, the cluster is asymmetric with 20 facets of different sizes. Fig. 7 shows an instantaneous configuration of the Ih gold cluster at  $T = 200\text{K}$ . We calculate the local curvature for each surface atom and color the atom according to the maximal local curvature. Fig. 7a shows this curvature coloring. Almost all of the atoms with large local curvatures are on the edges, yet those on the facets are with very small ones. Some atoms on the vertices are with very large local curvatures, but others are not. This is because some vertices lose their top atoms and form a small local flat region.

We then compute the local bond order parameters for all atoms. For a given atom, the bond order parameters calculations are performed on the neighboring geometry. The surface layer and the two sub layers closest to the surface have surface reconstruction and frozen in surface fluctuations, so we peeled them away, by the cone algorithm, to show clearly the structure in the bulk of the cluster (Fig. 7b). This coloring clearly marks the fcc  $\{111\}$  facets, the hcp edges, and the vertices with 5-fold symmetry.

## B. Melting behavior

We then heated up the cluster using constant temperature MD instead of the Andersen thermostat, so that the momenta are conserved to be 0 to simplify the analysis of dynamical properties. We still took the temperature intervals of 100K when far from  $T_m$ , but smaller when approaching it. At each temperature the system equilibrated for  $10^6$  steps (4.3ns), followed by  $10^7$  steps (43ns) to collect data.

In Fig. 8 we show the caloric curve (potential energy vs. temperature) of our 2624 atom gold cluster. At  $T = 1075\text{K}$  in our simulation range of 43ns the system has a first order transition from solid to liquid. That means by our heating procedure we found  $T_m = 1075\text{K}$ . However, after we equilibrated the system at  $T = 1070\text{K}$  for more than 240ns it also melted. We believe the exact  $T_m$  is still a little lower than 1070K. So at least in the time range of our simulation, the extraordinary stability of fcc  $\{111\}$  gold facets causes the superheating of the gold cluster, which also exists in slab-like fcc  $\{111\}$  gold surface<sup>23</sup>. It is also apparant that at  $T = 1050\text{K}$  the curve changed its slope, which suggests some phenomena more than thermal expansion begin to happen at that temperature.

We performed the cone algorithm recursively on the configurations to group atoms into layers. The outmost atoms are identified as surface layer, those immediately below surface layer are called the first sub layer, then the

second sub layer, and so on. There are totally 9 such layers for this 2624-atom system, and we label the atoms lying below the fourth sub layer as “interior” atoms. The number of atoms on each layer is shown in Tab. II. This layer dividing method looks arbitrary, but we can see from the following results that the sub layers all behave differently, suggesting that the sub layers as deep as the fourth one have surface effects. We could have stipped out more sub layers from the bulk, but as listed in Tab. II, only 220 atoms left for the bulk. Fewer atoms in the bulk and the extra sub layer might show results with interesting physical phenomena submerged in poor statistical fluctuations.

Then we used the bond orientational order parameters  $Q_4$ ,  $\hat{W}_4$ ,  $Q_6$  and  $\hat{W}_6$  together to check the structural change of the layers and the bulk. Because Ih clusters are macroscopically with icosahedral structure, yet locally with fcc, hcp and other structures, the global averaging bond order parameters are not exactly the values for a 13-atom icosahedron shown in Tab. I. In Fig. 9f we show the bond order parameters averaged over all the bonds between interior atoms. We see up to 1000K, the parameters keep their values corresponding to the icosahedral structure at low temperatures. Then they decrease their absolute values at 1050K-1070K just below  $T_m$ . With a sharp drop at  $T_m$ , all four turn to 0 demonstrating the liquid states. In contrast, Fig. 9a shows the bond order parameters averaged over the bonds only between the surface atoms. Now the bonds are roughly on a two dimensional surface, so the bond order parameters are different from those of the interior. Unlike Fig. 9f, we see a slow but pronounced decrease of  $Q_6$  and  $\hat{W}_6$ , starting at the temperature as low as just above 600K, and up to 1000K. At 1050K-1700K, they drop drastically towards, but do not reach 0. This measurement suggest that the surface softens gradually with the temperature approaching  $T_m$ , but do not completely melt below  $T_m$ . Other layers act trivially between the surface and the bulk, with smaller softening when the layer is closer to the bulk.

From the caloric curve and the bond order paramters plots we conclude that the Ih gold cluster with  $N = 2624$  has a sharp first order melting transition. With our simulation time of 43ns at each temperature,  $T_m$  is found to be 1075K. Yet it has been confirmed that the cluster is superheated in our simulation time scale, and the upper bound of actual  $T_m$  is 1070K. The bulk structure remains ordered up to  $T_m$  with small changes at 1060K and 1070K. The surface layer also remains ordered up to  $T_m$ , but with a noticeable softening beginning from about 600K. According to the bond order parameters calculations no surface premelting presented, and the bulk remains Ih structure as long as it is solid.

We have also considered how the definition of “bulk” effect our results. We redefine the “bulk” as with all atoms except those on the outmost two layers, and the bond order parameters plots shown in Fig. 10 behave almost the same as Fig. 9a except that the curves drop-

ping to zero are a little rounded, as we expected from the plots of others layers in Fig. 9. Thus our results and conclusions are insensitive to the detailed definition of surface and bulk.

From now on, wherever applicable, we exhibit plots and pictures at five typical temperatures: (1) 400K, representing the crystal at low temperature without interesting physical changes with temperature other than increasing thermal fluctuations; (2) 600K, when the surface starts to change (as we will show later some vertex atoms start to move at this temperature); (3) 900K, midway to  $T_m = 1075\text{K}$ ; (4) 1060K, just below  $T_m$ ; and (5) 1100K, just above  $T_m$ .

### C. Diffusion

Now let us consider the diffusion of atoms. Fig. 11 plots the average mean squared displacements defined in Eq. 16 and the diffusion coefficient  $D$  for the atoms initially on the surface layer, the sub surface layers, and the bulk.

All layers behave the same at 1100K because in liquid all of the atoms travel across the whole cluster no matter which layer they are initially on. At 400K the diffusion on all layers are almost negligible in the observation time of 20ns. At 600K the average diffusions on the surface layer and the first sub layer are roughly the same, the second layers diffuse slower, and other layers and the bulk behave essentially the same as at 400K. At 900K, the MSD plots of the three outmost layers increase quickly and then approach a value smaller than that of liquid. In contrast, other layers and the bulk have slow linear increasing. At 1060K, all layers qualitatively behave the same with slower diffusion rates when nearer to the bulk.

To follow the interlayer diffusion, at each temperature we label the atoms in the initial configuration by an integer  $n' = 0, 1, 2, \dots, 5$  according to whether the atom is on the surface, in the first sub layer, second sub layer, . . . , or interior of the cluster. At the end of the simulation for that temperature, we assign a new integer  $n$  to each atom, according to which layer the atom is now in. In Fig. 13 we plot  $\langle n \rangle$  vs.  $T$ , where  $n$  is averaged separately over each group of atoms indexed by their initial layer number  $n'$ . We see that significant interlayer exchanges take place between the surface and first sub layer, with these two layers roughly evenly mixed as much as 100 K below  $T_m$ . As  $T_m$  is approached, additional layers start to mix together. At  $T_m$  and above, all layers are evenly mixed during the course of the simulation.

It is quite interesting that at the temperature range from 600K to 900K, the diffusion of the first sub layer is larger than the surface layer. This is because at this temperature range, in the observation time of 20ns, some of the active atoms initially on the two layers just have enough mobility to jump to the other layer once, and stay on that layer to do the intralayer diffusion. Above that temperature range, the moving atoms can do inter layer

diffusion several times, so that the average diffusion of the two layers are almost the same.

The mobility of surface atoms is visually represented in the first row of Fig. 14 by the ellipsoids defined in Eq. 18. This representation gives us detailed information about the surface atom movements. In the observation time of 1.075ns, at 400K, the gold atoms only do thermal vibrations around their equilibrium positions, and no atoms move out of their crystal sites. At 600K, some vertex atoms move around about 2-3 atom distances. The movements of these very few vertex atoms contribute to the difference of the MSDs at 400K and 600K. At 900K, almost all of the vertex and edge atoms have significant moves with the biggest moves around the vertices, yet most of the atoms on the facets stay in their places. At 1060K just below melting, and 1100K just above melting, diffusion is pronounced throughout the entire surface, with the difference that at 1060K, a few facet atoms still stay unmoved. We increased the observation time and found that the ellipsoids larger than one atom distance grow in size.

### D. Average equilibrium shape

With the constant temperature MD, the angular momentum is conserved to be 0, which allows us to compute the average equilibrium shape at each temperature by the method specified in the method section. We divide space up into 842 approximately equal solid angles, corresponding roughly to the number of surface atoms. Over 1000 configurations sampled at equal times throughout the simulation time of 43ns have been averaged. The obtained equilibrium shapes are shown on the last two rows of Fig. 14. The pictures on the second row are the equilibrium shapes represented by the average positions in solid angles colored by their associating maximal local curvature. The pictures on the third row are the contour plots of the same shapes, and the view point is set to be finite in order to see clearly the change of the vertices and the edges.

At 400K, the vertices and the edges are sharp and the facets are quite flat. At 600K, the average shape is almost the same as at 400K, except some vertices are a little bit rounded. At 900K, the vertices and the edges are rounded significantly, and the facets are smaller. At 1060K, the facets almost shrink to nothing and the whole cluster has a rounded shape with some spikes on the surface. At 1100K, the equilibrium shape is a perfect sphere, as we expect for a liquid cluster.

### E. Roughness and curvature distributions

For all 1000 saved configurations over the simulation time of 43ns, at each temperature the bond curvature defined in Eq. 12, the roughness defined in Eq. 9, and the local curvatures defined in Eq. 15 (only maximal

local curvature is shown) have been computed. Their histograms are shown in the first row of Fig. 15. Because these histograms are based on the instantaneous configurations, the thermal fluctuations and statistical deviations play important roles. In liquid, the histogram of maximal local curvature is a distorted Gaussian distribution (due to the bias of picking the maximum), but those of bond curvature and roughness are  $\Gamma$  distributions, since no negative values are allowed in the latter cases.

At 400K, two peaks in the bond curvature histogram plot represent flat region and edge region respectively. We call the one near 0 the first peak, and the second peak for the other. We have expected a third peak to represent the vertices, but obviously it has been submerged in the tails of the former two peaks. With increasing temperature, while the center of the second peak remains unchanged, the first peak move to right, and both peaks become fatter due to the roughening of the facets. At 900K the second peak is overwhelmed by the first one, so that the valley no longer exists between two peaks. At 1060K, the curve can hardly be told as combined by two peaks. At 1100K the two peaks eventually coherent to be one perfect  $\Gamma$  distribution characterizing the statistics of the bond curvature in liquid state. The maximal local curvature and the roughness distributions act the same as the bond curvature, with less obvious second peaks.

Regarding the histograms at 1200K (the highest temperature we have) as the standard of the distributions in liquid, we compute the deviations of the histograms at each temperature away from that at 1200K and show them in the corresponding inner plots. The deviation is defined as the mean square root deviation of the difference between the two histogram values at the same point. All of the three show a continuous linear declination up to 1000K, with a slope change at about 1500K, and a quick dive down to the liquid value at about  $T_m$ .

The same procedure is also applied to the average shapes and they are shown in the second row of Fig. 15. Because now the thermal fluctuations are ruled out by the shape averaging procedure, the histograms are different from the above ones. At 400K, the bond curvature also has roughly two peaks. The first one very near to 0, representing the very flat facets without thermal fluctuations. The histogram has little change at 600K and 900K. At 1060K, the two peaks is too close to each other to be distinguishable, with a broad distribution centered about  $1/R$  with  $R = 21.5\text{\AA}$  the radius of the spherical liquid drop. At 1100K there is only one sharp peak centered at  $1/R$ , as the one in Fig. 5. The other two behave similar, while the first peak of the maximal local curvature at low temperatures centered exactly at 0 since the negative values are allowed, and two close peaks at 1060K of roughness represent respectively the spherical drop in liquid and the spikes on the sphere caused by unmoved atoms.

The deviations of bond curvature and maximal local curvature keep constant up to 1000K, with a slope change

at 1050K, and drop sharply to almost 0 at  $T_m$ . The deviation of roughness behaves similar, with a slow steady increasing at  $T \leq 1000\text{K}$ , suggesting that even with the thermal fluctuation averaged out, the surface of the average equilibrium shape becomes rougher when temperature increases.

Compared to the calibration results in Fig. 5, the results for the average shapes roughly have the same peak positions although the long tail of the first peak makes the second peak difficult to see. At low temperatures, the peak positions of the histograms for the instantaneous configurations are essentially the same as in Fig. 5 regardless the broad peak width, but this fact no longer holds at high temperature near and above  $T_m$ . Thus we learned that at high temperatures, the histograms for the instantaneous configurations contain more information of the fluctuation of the shape than the average properties of the shape.

The deviation plots of the histograms have the same characteristics as the caloric curve and the bond order parameters plots. Those results consistently suggest that no faceting transition separating from the first order bulk melting transition exists in the Ih gold cluster.

It is well known that near  $T_m$  the physical properties fluctuate significantly. So it is possible that near  $T_m$ , the real average shape might be perfectly rounded as in liquid, but our simulations of 43ns are not long enough to cover the fluctuations. To check this point, we have performed longer run with additional  $7 \times 10^7$  steps (301ns) at 1060K and 1070K with totally 8000 configurations sampled. As we averaged more and more configurations, we found the average shape does get rounder, but it only approaches to a limited value still far from the liquid. We quantify this rounding phenomena by the deviation computation as explained above and draw the time evolution of the deviation in Fig. 16.

## F. Other sizes

We also studied the cooling down of the gold clusters with the arbitrary sizes of 603 and 1409 atoms. Upon the same cooling down procedure, we also get the distorted Ih structure.

The melting behavior is studied for the above two sizes, as well as the constructed ideal Ih clusters (with a missing central atom) with the magic numbers of 560, 922, 1414, 2868, and 5082 atoms. While the melting temperature was observed to increase with increasing cluster size, we continued to find the same general features, with the surface softening tracking the increase in  $T_m$ . The only significant difference of the melting behavior between the clusters with magic numbers and non-magic numbers is that those with magic numbers are more stable on both surface and bulk.



#### IV. MECHANISM

From the above results we conceive a detailed mechanism of how the Ih gold cluster with 2624 atoms behave with temperature approaching  $T_m$ , effected by both the extraordinary stability of fcc {111} gold surface and the increasing mobility of the vertex and edge atoms. In return we use the concluded mechanism to reconcile the results we have obtained.

At  $T < 600\text{K}$ , despite of the change of the thermo vibration of the atoms constrained in their crystal sites, the cluster remains essentially the same. At  $T = 600\text{K}$ , some vertex atoms on the surface with least binding energy hop around the vicinity and exchange with the sub surface vertex atoms. This movement is captured by the ellipsoid representation in Fig. 14, and results in very little rounding of the vertices in the equilibrium shape. It also leads to the small change of the MSD in Fig. 11 a,b and the surface plot in Fig. 13.

With increasing temperature from 600K to 1000K, more vertex and edge atoms on the surface diffuse in the surface layer or jump into the first sub surface layer. The increasing mobility of these atoms release the constraint on the surface atoms near the vertices and edges as well as the vertex and edge atoms on the first sub layer, so that they also diffuse as well, which leads to the shrinking of the facets (900K in Fig. 14) and the increasing diffusion of the first sub layer. As the surface effect decreases with the depth, the mobility of the atoms beneath the first sub layer does not increase beyond the linear influence of the increasing temperature. (900K in Fig. 11). At about 1060K, the bulk become softer, and the facets on the surface almost shrink to nothing. The bond order parameters and other properties change a lot towards the liquid. However, a few surface atoms remain in their original places, so that those properties can not reach those of liquid, thus surface does not completely melt. The surface completely melts only when the temperature reaches the bulk melting temperature  $T_m$ .

#### V. SUMMARY AND CONCLUSIONS

Our cooling procedure for the three sizes of 603, 1409 and 2624 atoms all lead the systems to a Mackay icosahedral structure with a missing central atom. Due to the small size of the clusters, at high temperature, the shape fluctuates vibrately, so that the instantaneous configuration is always more faceted than the average. Our simulation verified the fluctuations are distributed around an equilibrium shape at each temperature.

With increasing temperature, vertex atoms start to diffuse first, the edge atoms diffuse at a little higher temperature, rounding the vertices and edges. Although surface atoms diffuse at lower temperature, the surface structure softens only about 100K below melting temperature. No surface melting prior to bulk melting has been observed in our simulation. The difference of melting behavior between Mackay icosahedral gold cluster and infinite fcc 111 surface is caused by the increasing mobility of vertex and edge atoms.

From all of the results we can also conclude that there is a faceting (or equivalently roughening) of the gold 111 surface of the cluster, that takes place as a finite size effect, and tracks the melting transition, occurring just below the melting. However, no evidence has been found of a faceting transition separated from the main bulk melting transition.

It would be interesting to know how this surface softening is related to morphological transitions observed in gold nanorods at temperatures below the melting temperature<sup>29,33</sup>.

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## TABLES

**TABLE I: Bond order parameters for face-centered-cubic (fcc), hexagonal close-packed (hcp), icosahedral and liquid structures.**

Geometry	$Q_4$	$Q_6$	$\hat{W}_4$	$\hat{W}_6$
fcc	0.19094	0.57452	-0.15932	-0.01316
hcp	0.09722	0.48476	0.13410	-0.01244
icosahedral	0	0.66332	0	-0.16975
liquid	0	0	0	0
fcc {111} surface	0.37500	0.74083	0.13410	-0.04626
fcc {110} surface	1	1	0.13410	-0.09306
fcc {100} surface	0.82916	0.58630	0.12497	-0.00721

**TABLE II: Average numbers of atoms on the surface layer, the sub layers and the bulk of a N=2624 gold cluster at different temperatures.**

$T$	Surface	Sub layer 1	Sub layer 2	Sub layer 3	Sub layer 4	Bulk
400K	$858.5 \pm 0.6$	$602.8 \pm 0.8$	$428.3 \pm 1.1$	$307.4 \pm 1.1$	$207.2 \pm 0.8$	$219.6 \pm 1.$
600K	$859.8 \pm 1.2$	$602.2 \pm 1.4$	$427.9 \pm 1.2$	$307.3 \pm 1.1$	$207.2 \pm 0.9$	$219.7 \pm 1.$
900K	$867.7 \pm 2.4$	$594.9 \pm 2.6$	$427.5 \pm 1.4$	$307.0 \pm 1.2$	$207.0 \pm 1.0$	$219.9 \pm 1.$
1060K	$869.9 \pm 3.6$	$582.4 \pm 4.0$	$436.2 \pm 3.2$	$311.3 \pm 2.6$	$208.6 \pm 2.2$	$215.7 \pm 3.$
1100K	$874.7 \pm 3.9$	$572.4 \pm 4.2$	$436.2 \pm 4.2$	$308.7 \pm 4.0$	$209.9 \pm 3.7$	$222.1 \pm 5.$

## FIGURE CAPTIONS

1. Scheme of the cone algorithm.
2. Scheme of the bond curvature.
3. Scheme of the local curvature fitting.
4. Intersections of an Ih gold cluster with 2624 atoms at (a)  $T = 200\text{K}$  (Ih) and (b)  $T = 1200\text{K}$  (liquid) with the layers divided by the cone algorithm and marked by different gray scales.
5. Bond curvature, maximal local curvature and roughness histograms of the constructed Ih gold cluster (the configuration shown in Fig. 7c) in the first row and of the liquid average shape (shown in Fig. 6c) in the second row.
6. Average shape of liquid gold with 2624 atoms at  $T = 1200\text{K}$ . (a) Four instantaneous configurations. (b) Distribution of Surface atom positions from 1000 configurations proejcted on the xz plane. Each atom position is shown as a small dot. (c) Average equilibrium shape.
7. Ih structure of  $N = 2624$  at  $T = 200\text{K}$ . (a) Surface of an instantaneous configuration shaded by maximal local curvature with the darker the larger curvature. (b) The same configuration with three outmost layers peeled away. Atoms are shaded according to their local structure: fcc is white, hcp is gray, and other is black. The surface of a constructed ideal Ih gold cluster with the magic number of 2868 (with a missing central atom) is shaded by the maximal local curvature and shown in (c) for comparison.
8. Caloric curve of 2624 atom Ih gold cluster.
9. Bond orientational order parameters for (a) surface layer, (b) first sub layer, (c) second sub layer, (d) third sub layer, (e) fourth sub layer, and (f) interior.
10. Bond orientational order parameters of the “interior” defined as all atoms below the first sub layer.
11. Mean squared displacements averaged over atoms in (a) surface layer, (b) first sub layer, (c) second sub layer, (d) third sub layer, (e) fourth sub layer, and (f) interior.
12. Diffusion coefficients  $D$  vs.  $T$  in different layers. The inner plot is the zoomed picture of  $D$  at the temperature range of 700K-1050K.
13. Inter layer diffusion of atoms.
14. Curvature, roughness and equilibrium shape at 400K, 600K, 900K, 1060K and 1100K. (a) Ellipsoid representation of root mean square displacements of surface atoms with the simulation time of 1.075ns. (b) Average equilibrium shape with the simulation time of 43ns. The particles represent the average atom positions in solid angles, not the real surface atoms. (c) Contour plot of (b) with viewpoint at finite to see clearly the rounding of vertices and edges.
15. Bond curvature, maximal local curvature and roughness histograms and mean square root deviations of the instantaneous configurations (first row) and average shapes (second row). (a) Bond curvature. (b) Maximal local curvature. (c) Roughness.
16. Time evolution of the deviation of the average shape from liquid at 1060K and 1070K.