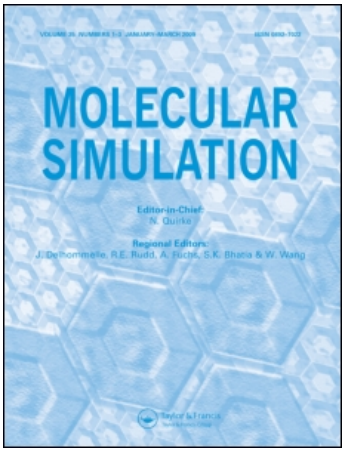

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Dissociation of Au_n (n = 3, 4) Microclusters

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Preliminary Communication

DISSOCIATION OF Au_n (n = 3, 4) MICROCLUSTERS: A MOLECULAR DYNAMICS SIMULATION

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The dissociation of Au_3 and Au_4 microclusters has been investigated using a molecular-dynamics computer simulation. The potential energy function used in the calculations includes two- and three-body interactions, which are represented by Lennard–Jones and Axilrod–Teller potentials, respectively. It has been found that dissociation starts for both clusters after 3000K.

KEY WORDS: Gold, microcluster, dissociation, molecular-dynamics, potential energy function.

The investigation of the properties and dynamics of small clusters is a rapidly expanding field. These aggregates of atoms and molecules which are held together by all types of forces, ranging from weak Van der Waals and hydrogen bonding to strong metallic covalent and electrostatic forces play a crucial role in nucleation, crystal growth, catalysis, adsorption and increasingly in new materials and devices. Experimental and theoretical work [1–15] has been undertaken to explore and understand the nature of the small clusters. Some of the work on the subject is mainly concerned with calculating the minimum energy structure of the cluster (at 0 K or at 1 K) [1, 3, 6, 13–15], the rest is concerned with ordinary normal mode analysis to determine the temperature dependence of the cluster properties [4, 5, 11, 12].

In the light of the previous studies, it is now clear that, microclusters are not necessarily those of the bulk material and melting takes place between an ordered microcluster phase and a liquid phase [11, 12]. On the other hand simulation studies have also shown qualitative differences between the melting of clusters having different number of atoms [4, 5, 11, 12]. The structural properties of Au_n microclusters with the number of atoms n = 3 to 7 have been investigated recently [13], and the most stable configurations have been determined by using Molecular Dynamics (MD) technique. The energetically most stable configurations of Au_3 and Au_4 microclusters were found at (1 K) to be triangular form with D_{3h} symmetry and tetrahedral configuration with T_d symmetry, respectively.

In the present work the dissociation mechanism of Au_3 and Au_4 clusters has been investigated as first time by using a MD simulation. The starting geometry of these clusters has been taken as the most stable structure of the previous work [13]. The potential energy function, which is the combination of Lennard–Jones and Axilrod–Teller potentials, and the necessary parameters used here are the same as in reference 13. The details of the potential functions and the MD procedure may also be found

in reference 13. (In this potential the interaction range between any two atoms, called cut-off radius (R_c), is taken as 6.66 Å.)

During the simulation the system is thermally equilibrated at a given temperature. It is found that 7000 MD steps (each time step is 1.4×10^{-15} sec.) was sufficient to reach thermal equilibrium; in the first 5000 steps temperature rescaling is applied and in the last 2000 steps the system is allowed to relax. This process is defined as "one run of the MD simulation." In each MD run the temperature is gradually increased up to 1000 K by steps of 200 K and then up to 3000 K by steps of 100 K. As the fluctuation in the interatomic distances increases after 3000 K; beyond this limit, the increment in the temperature rise is taken as 50 K.

Total interaction energy (TIE) of the clusters versus temperature (T) is given in Figure 1. In the case of Au_3 cluster, the decrease in TIE within the temperature range of 1–3000 K is about 0.15 eV leading to an almost constant TIE. After 3000 K, the relative position of one of the atoms in the cluster changes considerably with respect to the others, and at 3150 K the distance of this atom to the other two atoms exceeds R_c. This is interpreted as the dissociation of this cluster. The fluctuation in the interatomic separation of the remaining two atoms is relatively very small. The first dissociation stage of Au_3 may be expressed as

$$Au_3 \rightarrow Au_2 + Au \qquad (\text{at } T = 3150\,\text{K}) \tag{1}$$

The difference in average interaction energy per atom before and after dissociation is about 0.35 eV.

On the other hand, Au_4 cluster shows a different characteristics. TIE varies again smoothly between 1–1700 K, the total decrease in this temperature range being 0.15 eV. However, the change in the interatomic distances between 1700–3500 K looks like as if Au_4 is formed by two dimers which are fluctuating with respect to each other. From this behaviour one would expect that Au_4 could separate into two dimers at the first dissociation stage, but at 3500 K instead of this expectation only one of the atoms in Au_4 leaves the system (similar to Au_3) as follows

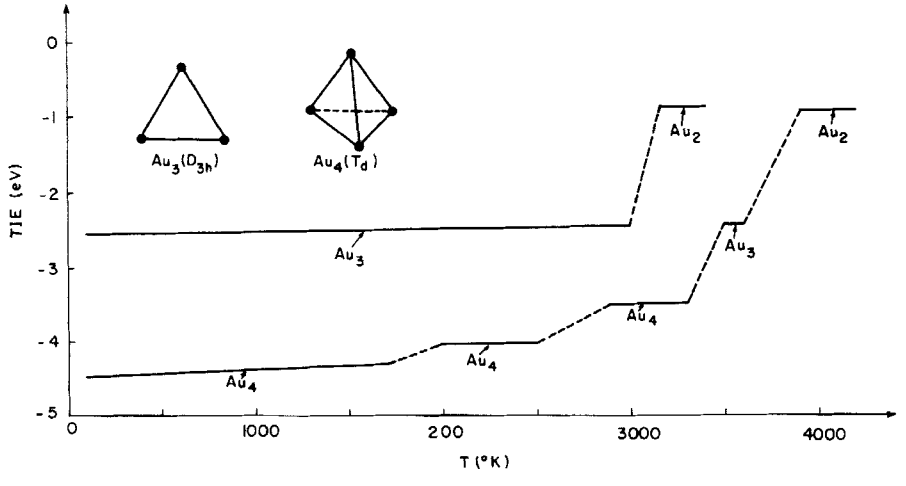

Figure 1 Total interaction energy (TIE) versus temperature (T) for Au_n (n = 3, 4) microclusters. Dashed lines show the regions where fluctuation in interatomic distances is large.

$$Au_4 \rightarrow Au_3 + Au \qquad (\text{at } T = 3500\,\text{K}) \tag{2}$$

The TIE of the product Au_3 in Equation 2 is almost the same as the TIE of the Au_3 in Equation 1, as expected. This situation is seen in the figure clearly. The difference in average interaction energy per atom before and after the first dissociation is about 0.06 eV.

The second dissociation of Au_4 (or the first dissociation of the product Au_3 in Equation 2) takes place at 3900 K. The TIE versus T characteristics of product Au_3 between 3600–3900 K shows the same behaviour of Au_3 cluster. The first and second dissociation stages of Au_4 cluster may be expressed as follows

$$\begin{aligned} Au_4 &\rightarrow Au_3 + Au \qquad (\text{at } T = 3500\,\text{K}) \\ &\downarrow \\ Au_3 &\rightarrow Au_2 + Au \qquad (\text{at } T = 3900\,\text{K}) \end{aligned} \tag{3}$$

The final product dimers (Au_2) of both clusters Au_3 and Au_4 almost have the same interaction energy of ~ 0.9 eV, as expected. The difference in average interaction energy per atom before and after the second dissociation of Au_4 cluster is about 0.35 eV. Since the temperature increments are taken at T (= 50 K) steps after 3000 K, it would be better that the dissociation temperature states in Equations 1–3 may be assumed as the average dissociation temperatures of the clusters.

The first dissociation stage of Au_4 takes place at a higher temperature than that of Au_3. The situation is expected because the number of bonds to break in a larger cluster is more than that of a smaller one; this means that more energy is required. This result is in agreement with the fact that the melting temperature increases as cluster size increases [11, 12]. Consequently, the present calculation gives a qualitative information about the dissociation mechanism of gold microclusters, which may be important for experimental investigations.

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