Revista Mexicana de Física
ISSN: 0035-001X
rmf@ciencias.unam.mx
Sociedad Mexicana de Física A.C.
México

Ruíz Gómez, J.C.; Rincón, L.
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Revista Mexicana de Física, vol. 53, núm. 7, diciembre, 2007, pp. 208-211
Sociedad Mexicana de Física A.C.
Distrito Federal, México

Melting of intermediate-sized gold nanoclusters

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Recibido el 30 de noviembre de 2006; aceptado el 8 de octubre de 2007

In the present work, the melting behavior of nanometer-sized gold clusters using the Sutton-Chen potential is studied. We calculated the temperature dependence of the potential energy from 50 K to 1100 K for different sizes of clusters (13 to 2869 atoms). The dependence of the melting temperatures with the size of the clusters follows the Pawlow formula.

Keywords: Nanocluster; semiempirical; Au; melting.

En este trabajo se estudia el comportamiento de la fusión de nanoagregados de oro usando el potencial de Sutton-Chen. Se obtiene dependencia de la energía potencial con la la temperatura en el rango de 50 a 1100 K para nanoagregados de diferentes tamaños (de 13 a 2869 átomos). La temperatura de fusión versus el número de átomos de los nanoagregados sigue la fórmula de Pawlow.

Descriptores: Nanocluster; semiempirical; Au.

PACS: 61.46.Hk; 78.30.-j; 78.55.Et

1. Introduction

Nanoclusters are of fundamental interest due to their own intrinsic properties and because of the central position that they occupy in molecular and condensed matter science. Nanoclusters 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 large range of applications, such as nanolithography [1], catalysts [2], nanobioelectronic devices [3] and ion detection [4]. Molecular dynamics simulations have shown [5] that the gold clusters with about 600-3000 atoms crystallize into a Mackay icosahedron (Ih) upon cooling from liquid. Different theoretical and numerical models have indicated different limits for the stability of such Ih clusters. In the present work, the melting behavior of nanometer-sized gold cluster was studied using the Sutton-Chen potential [6]. We calculated the temperature dependence of the potential energy from 50 k to 1100 K for clusters of different sizes (13 to 2869 atoms). An exhaustive search for the minimum energy structure for intermediate-sized clusters is out of question, owing to the exponential increase in the number of nearly equivalent local energy minima.

2. Melting of nanoclusters

The concepts of solid and liquid states, which are commonly employed when discussing extended systems, can be applied to clusters. In fact, at a low temperature, the particles of a cluster spend most of the time making small-amplitude vibrations around global minimum, in analogy to what happens in bulk solids. If the temperature is increased, other minima begin to be populated, and this is associated with the onset of some diffusive motion. Finally, if the temperature becomes high enough, the cluster explores the basin of a huge number of minima, with fast rearrangements, thus behaving like a liquid droplet. Within this description, cluster melting is seen as an isomerization transition, with the number of probable isomers increasing drastically after some threshold temperature.

3. Simulation model and methods

In this paper we simulated, by molecular dynamics (MD), the freezing of gold clusters from the liquid and the reheating the clusters back through the melting transition T_m. We apply a simulated annealing in the former stage and then simulated heating in quasiequilibrium, running for a simulated time of $2 \times 10^5 fs$ at each temperature before increasing the temperature. The melting temperature is achieved from the change in the slope of the caloric curve.

3.1. Molecular dynamics

The molecular dynamics simulation was carried out using the oopse [7] program. We used the Sutton-Chen potential [6], in which the total potential energy is expressed as:

$$U_{tot} = \sum_i \left[\frac{1}{2} \sum_{j \neq i} D_{ij} V_{ij}^{pair}(r_{ij}) - c_i D_{ii} \sqrt{\rho_i} \right] \quad (1)$$

where V_{ij}^{pair} and ρ_i are given by:

$$V_{ij}^{pair}(r_{ij}) = \left(\frac{\alpha_{ij}}{r_{ij}} \right)^{n_{ij}} \quad (2)$$

$$\rho_{ij} = \sum_{j \neq i} \left(\frac{\alpha_{ij}}{r_{ij}} \right)^{m_{ij}} \quad (3)$$

V_{ij}^{pair} is a repulsive pairwise potential that accounts for interactions of the pseudo-atom cores. The $\sqrt{\rho_i}$ term in equation 1 is an attractive many-body potential that models the interactions the valence electrons and the cores of the pseudo-atoms. D_{ij}, D_{ii}, c_i and α_{ij} are parameters used to tune the potential for different transition metals.

The method used for integrating the equations of motion is a velocity-Verlet version of the symplectic splitting method [8]. The integration step Δt is of $4.3\ fs$. The simulations are carried out in the NVT ensemble using the $Nosé - Hoover$ [9] thermostat.

3.2. Simulated annealing

Beginning at a temperature around 1200 K, we let the clusters evolve for an interval of $2.0 \times 10^5 fs$ at each temperature and then decreased the temperature 10% each time. This process is repeated until the clusters reached a temperature around 50 K.

3.3. Quasiequilibrium heating process simulation

The last structure the clusters obtained after the simulated annealing is used as a starting geometry for the heating process. We begin with a temperature of 50 K and let the clusters evolve for an internval of $2.0 \times 10^5 fs$ at each temperature. Then the temperature is raised by an amount of 50 K each time until a temperature of 1100 K is obtained.

4. Calculation of melting temperature

The method used for studying the melting transition is the calculation of the caloric curve (average potential energy U per atom versus temperature), by heating the clusters from a low temperature solid configuration to a melted state. U shows a smooth jump in the melting region, corresponding to a peak in the heat capacity $c(T) = \partial U/\partial T$. For the cases of small clusters, multiple peaks in the heat capacity curve are observed. These peaks are associated with a change in structure in the clusters.

5. Size dependence of the melting point

The size dependence of the cluster melting point for a given material usually shows a monotonic decrease with decreasing size and has an irregular variation in a fine scale. Here the Pawlow's formula [10] is derived following the approach of Buffat and Borel [11]. Consider a cluster of size N and of spherical shape. At a given pressure p, its melting point is $T_m(N)$, which has to be compared with the bulk melting temperature $T_m(\infty)$. When the solid-liquid transition takes place, the chemical potentials μ_s and μ_l of the solid and the liquid must become equal, so

$$\mu_s(p,T) = \mu_l(p,T) \tag{4}$$

Expanding the chemical potential around its value at the triple point, and retaining first order terms only:

$$\mu_s(p,T) = \mu_s(p_0,T_0) + \frac{\partial \mu}{\partial T}(T-T_0) + \frac{\partial \mu}{\partial p}(p-p_0) \tag{5}$$

from the Gibbs-Duhem equation ($-Vdp+SdT+Nd\mu = 0$) it follows that

$$\frac{\partial \mu}{\partial T} = -s, \qquad \frac{\partial \mu}{\partial p} = \frac{1}{\rho} \tag{6}$$

where $s = S/N$ is the entropy per particle and $\rho = V/N$ is the number density. From Eqs. 4-6 and by taking into account that $\mu_s(p_0,T_0) = \mu_l(p_0,T_0)$, we have:

$$-s_l(T-T_0)+\frac{1}{\rho_l}(p_l-p_0) = -s_s(T-T_0)+\frac{1}{\rho_s}(p_s-p_0) \tag{7}$$

The pressure inside a small object of radius r is larger than the external pressure because of the Laplace contribution $p_{Lap} = 2\gamma/r$, where γ is the interface tension of the cluster and r is its radius.

$$p_l = p_{ext} + \frac{2\gamma_{lv}}{r_l}, \qquad p_s = p_{ext} + \frac{2\gamma_{sv}}{r_s} \tag{8}$$

(the subscripts s, l and v stand for solid, liquid and vapor, respectively). For clusters of $r \sim 10\ nm$, $p_{Lap} \gg p_{ext}$. Moreover, for spherical clusters,

$$\frac{r_s}{r_l} = \left(\frac{\rho_l}{\rho_s}\right)^{1/3} \tag{9}$$

By substituting Eqs. 8 and 9 into Eq. 7, neglecting p_{ext}, and taking into account that $L = T_0(s_l - s_s)$ is the latent heat of melting per particle, one obtains

$$1 - \frac{T_m(N)}{T_m(\infty)} = \frac{2}{\rho_s r_s L}\left[\gamma_{sv} - \gamma_{lv}\left(\frac{\rho_s}{\rho_l}\right)^{2/3}\right] \tag{10}$$

Since $r_l \propto N^{1/3}$ Eq. 10 can be rewritten as

$$T_m(N) = T_m(\infty)\left[1 - \frac{C}{N^{1/3}}\right] \tag{11}$$

6. Results

In this section we report our results. We simulate the melting of gold clusters of different sizes (13, 55, 147, 309, 561, 923, 1415, 2057 and 2869 atoms) and that of the bulk gold. Clusters with less than a few hundred atoms have large finite size effects due to the larger surface-to-volume ratio; they have less sharply defined melting transitions. In Fig. 1 we show the caloric curve and the specific heat for the clusters, and in Fig. 2 we show the bulk counterpart. The bulk system is simulated imposing periodic contour conditions to a system composed of several hundred atoms. The melting temperature is obtained locating the (first) peak in the heat capacity curve.

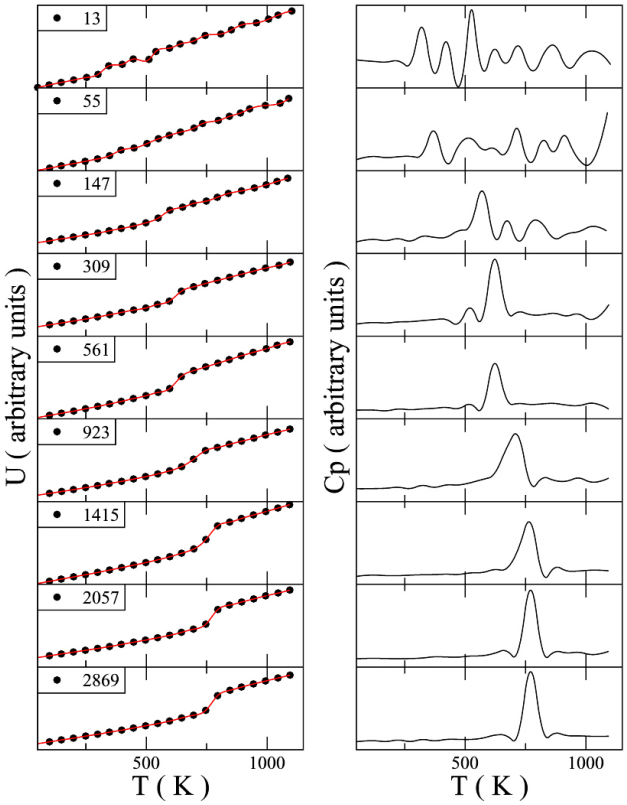

FIGURE 1. Caloric curve and specific heat of the clusters of different sizes.

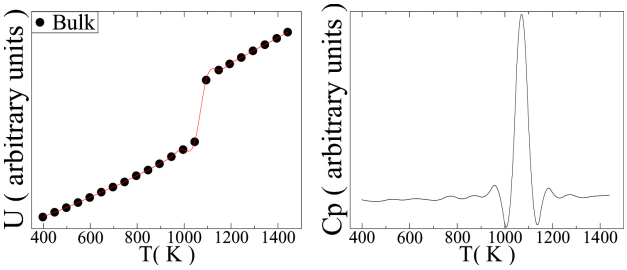

FIGURE 2. Caloric curve and specific heat of the bulk.

In Fig. 3 we show the radial distribution of the atoms from the cluster center of mass. This helps us distinguish the ordered states from the disordered ones. This information reinforces the melting point data obtained from the specific heat curve.

In Fig. 4 we show the meting temperature T_m vs. the number of atoms N, and we also present two fits for this data. We use the Pawlow model for fitting the obtained melting points. When we fix $T_m(\infty)$ to the experimental melting temperature of bulk gold 1337.58 K, the fitting cannot adjust to the obtained data. If we use $T_m(\infty)$ as a free parameter, we obtain a value of 894 K for the melting point of the bulk gold and the fitting adjusts to the obtained melting points of the clusters.

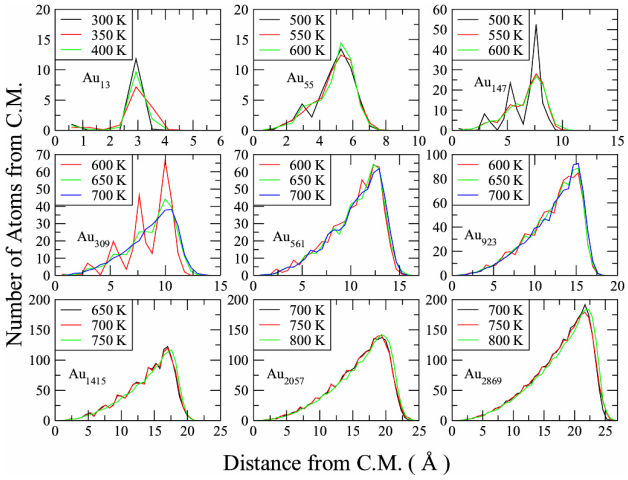

FIGURE 3. Radial distribution of atoms from the cluster center of mass.

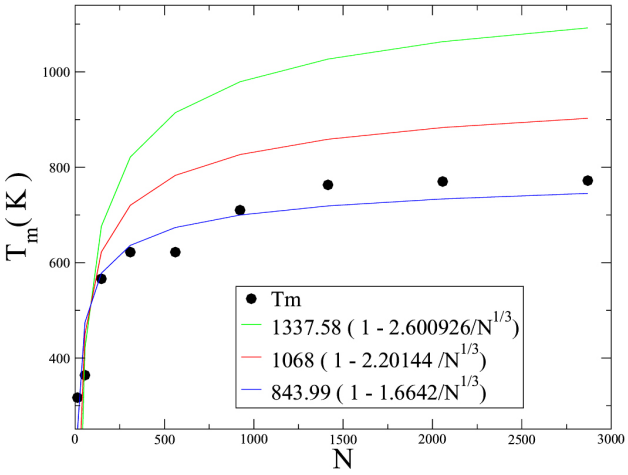

FIGURE 4. Melting temperature T_m and three fits vs the number of atoms N.

7. Discussion and conclusions

From the caloric curve (Fig. 1) it can be noted that for the smaller clusters, the melting process occurs in a wide range of temperatures; this range of temperature becomes narrower when the size of the cluster is increased. Furthermore, there are many peaks in the specific heat curve that may be associated to changes in the structure. In these cases, the peaks have similar sizes. We think that even though there are many structure transitions in these cases, the number of available states at a given temperature is not as large as in the cases of bigger clusters. When the size of the clusters is sufficiently large, a very large number of states suddenly appears in the melting region, so the melting process is sharper than in the case of smaller clusters. This analysis can be complemented by the inspection of Fig. 3. When the temperature is below the melting temperature, we can note peaks in the radial distribution of atoms from the center mass of the clusters; we associate this behavior with a shell structure. If the temperature is increased above a certain value, these peaks dissappear

and the distribution of atoms for the center of mass becomes softer than before. This fact is associated with the fusion of the clusters. Finally, when we use the Pawlow model to fit our data, a large discordance is observed using the experimental bulk melting temperature $T_m(\infty)$, perhaps due to the fact that the bulk melting temperature in the Sutton-Chen potential (1068 K, see Fig. 2) is different than the experimental one. The situation is improved when the "Sutton-Chen bulk melting temperature is used". We obtain the best concordance using $T_m(\infty)$ as a free parameter; in this case, we obtain a bulk meting point of 893 K. This situation may be attributed to (the combination of) several factors:

(1) The absence of a sharp definition of a melting point for small clusters: we could choose erroneous values for the melting points

(2) The fact that the starting configurations are not of the absolute minimal energy: there is a probability of attaining structures of lower energy when raising the temperature of the clusters

(3) Inherent limitations of the Pawlow model and the used potential.

Acknowledgments

We would like to thank CDCHT and CEP of the Universidad de Los Andes-Venezuela, and the Consejo de Investigación of the Universidad de Oriente-Venezuela for their financial support.

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