

# Structural transitions and melting of copper clusters

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**Abstract.** Molecular dynamics is used to study the melting and structural transitions of small copper clusters. The melting temperature is found to be proportional to the average coordination number. Small icosahedral clusters melt at slightly higher temperatures than the cubic structures. Small cuboctahedral clusters are not stable but transform via a nondiffusive transition to icosahedral structure.

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## 1. Introduction

The phase stability of small clusters is different from that of the infinite matter. The ground state geometries of small clusters differ drastically from the bulk crystalline material. In the smallest metal clusters the ground state geometry is governed by the electronic shell structure[1–3] whereas in large clusters the tight packing of atoms, especially on the surface, seem to dominate the structure[4–6]. Consequently, clusters consisting of hundreds of atoms seem to prefer icosahedral packing as compared to any cubic structure. Experimental results for rare gas clusters[7] as well as for many metal clusters[8] have confirmed the existence of icosahedral clusters. Many other geometries are also stable at low temperature and it is then important to know how easily they can transform from one to another[9].

The melting temperature of the small clusters is smaller than the melting temperature of the bulk metal[10, 11]. The melting of small clusters rises many interesting phenomena: How does the melting temperature depend on the clusters size? Does the melting temperature depend on the geometry? Can the clusters be superheated? In the present work we have studied these questions using molecular dynamics (MD) for copper clusters.

The total energy of the metal is described with many-atom potentials of the effective medium theory[12, 13] and a standard MD method is used to study the

dynamics of the cluster. The technical details as well as more results will be published elsewhere[14].

## 2. Instability of small cubic clusters

Each cluster size  $N$  has a specific ground state geometry determined by minimizing the total energy. Using computer simulations it is easy to obtain stable local energy minima which are not the ground state. These structures can transform to other structures when the cluster is heated. The stability of the geometry will determine if the cluster can grow in that form or if it will transform into another geometry. During our melting simulations we have obtained transformations which will be discussed below.

The cuboctahedron transforms to an icosahedron via a nondiffusive transition[4, 15]. In small clusters this transformation does not have any activation barrier, as demonstrated in Fig. 1 where the total energy as a function of simulation time is shown for a 147 atom cluster. Initially the cluster is a cuboctahedron quenched very fast from 300 to 0 K by stopping each atom whenever it starts to decelerate. In the relaxed 'minimum' energy structure the atoms start slowly to move out from their nearly exact cuboctahedral sites and soon the cluster collapses into an icosahedron. In the dynamical simulations the smallest clusters can oscillate between the icosahedral and the cuboctahedral structure[16].

Cubic geometries other than the cuboctahedron are in general more stable against transformations to icosahedral shape. Large Wulff polyhedra which have smaller (100) facets than the cuboctahedra seem to stay in cubic structures all the way to the melting temperature. A similar result was obtained for a large octahedral cluster (891 atoms). However, in simulations the heating rate of the cluster is usually very fast as compared to any time constants in experiments, and transition which require considerable amount of diffusion can not be observed in MD simulations.

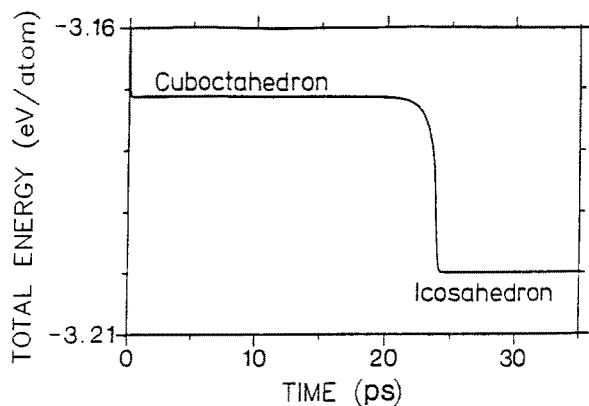


Fig. 1. Total energy as a function of time for a 147 atom cluster. The originally cuboctahedral structure relaxes to an icosahedron without an activation barrier.

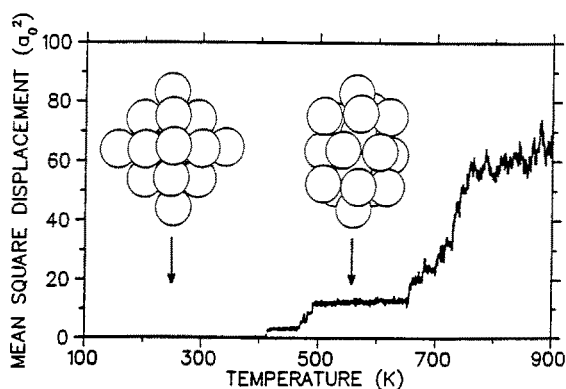


Fig. 2. Mean square displacement of a 19 atom cluster as a function of the temperature. The cluster is originally an octahedron but transforms to an icosahedral structure during heating.

Figure 2 demonstrates a transformation observed in a very small cluster. The 19 atom octahedron transforms at a relatively low temperature to an icosahedron with a partially filled outermost shell. The Wulff polyhedron of 38 atoms transforms also into an other structure before the melting temperature. Also this structure might to be related to the icosahedral structure, but a detailed analysis was not made. When the cluster size increases more and more diffusion is needed for the cubic structure to change into an icosahedral structure (except for the cuboctahedron) and consequently these transitions are difficult to observe using MD. For clusters smaller than about 2500 atoms the icosahedral clusters have the lowest ground state energy whereas for larger clusters the Wulff polyhedron seems to be the ground state.

### 3. Melting of copper clusters

The melting of copper clusters with different geometries were studied by heating the clusters with a constant rate (2.5 K/ps) and monitoring the total energy and mean square displacement of atoms as a function of the temperature. Figure 3 shows the melting temperature

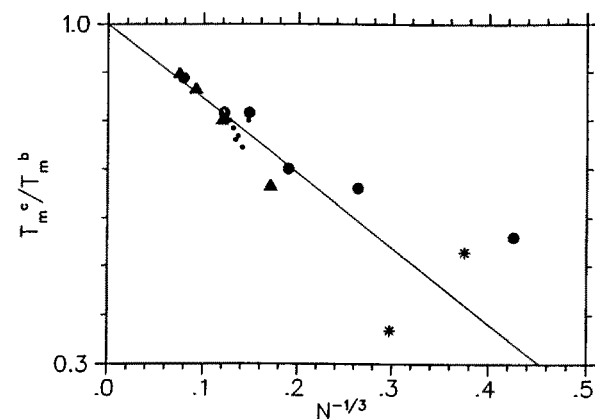
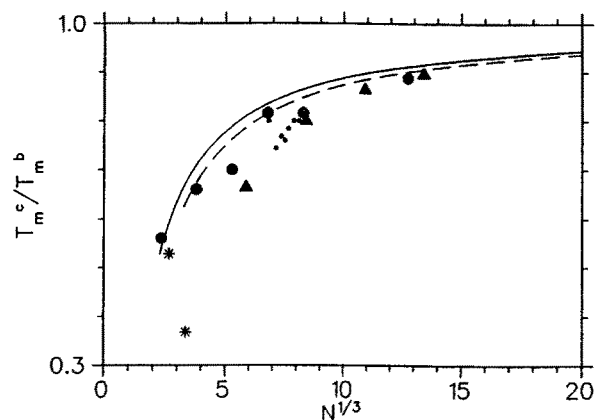


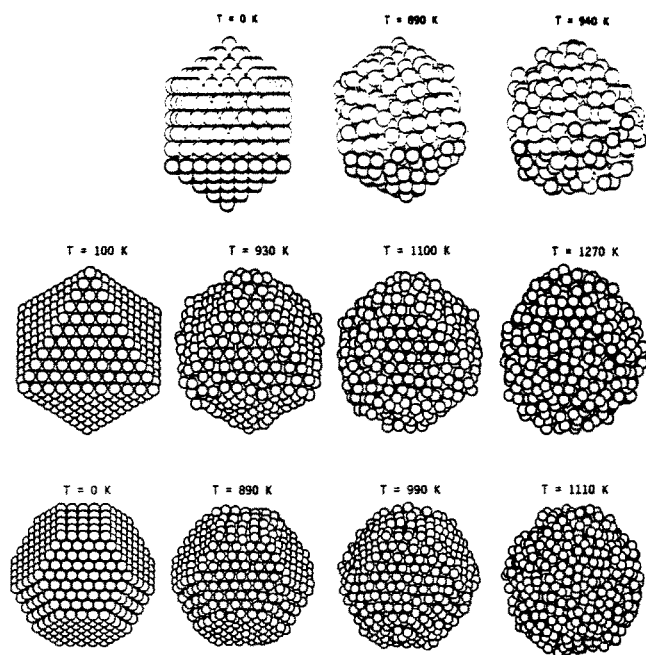
Fig. 3. Melting temperature as a function of the cluster size. Large and small black dots denote closed and open shell icosahedra, respectively. Triangles denote Wulff polyhedra and stars small Wulff polyhedra which transformed to an other structure before melting. Solid and dashed lines are estimates based on the mean coordination number for icosahedral and Wulff polyhedral clusters, respectively.

as a function of the number of atoms in the cluster. Icosahedral clusters (black balls) melt, on average, at slightly higher temperatures than the cubic clusters with a geometry of the Wulff polyhedron (triangles). This difference could be partly due to the overheating which is easier in the icosahedral cluster due to the very tight surface structure[13].

The reduction of the melting temperature can be explained with the reduction of the average coordination number of atoms in the cluster. The Lindemann criterion gives an estimate for the melting temperature of the cluster as

$$T_m^c = C_c T_m^b / C_b, \quad (1)$$

where  $T_m^b$  is the melting temperature of the infinite system (our potential gives  $T_m^b = 1240$  K [17]) and  $C_c$  and  $C_b$  are the average coordination numbers in the cluster and in the bulk, respectively. Figure 3 shows that Eq. (1) gives a reasonable estimate for the size dependence of the cluster melting temperature.



**Fig. 4.** Examples of cluster structures at low temperatures, just below the melting and after the melting. From up to down: 360 atom open shell icosahedron (the open shell atoms are denoted by thicker lines), 891 atom octahedron and 1289 atom Wulff polyhedron.

Thermodynamical approach based on the surface and volume free energies gives the size dependence[14]

$$T_m^c = T_m^b - KN^{-1/3}, \quad (2)$$

where  $K$  is a constant. Figure 3 shows that the  $N^{-1/3}$ -dependence is verified by the MD simulations.

Figure 3 also shows the melting temperatures of some icosahedra with a partially filled outermost shell (small black dots). These seem to melt at slightly lower temperatures than the complete icosahedra. It should be kept in mind, however, that each point in Fig. 3 corresponds to only one simulation and in obtaining an accurate melting temperature a large number of simulations for each size should be made.

Figure 4 shows examples of cluster structures just below and above the melting temperature. In all cases no reconstruction of the cluster is seen before the melting. In the case of the incomplete icosahedron (Fig. 4a) the whole cluster melts simultaneously without any surface premelting. In the 1289 atom Wulff polyhedron the (100) faces seem to disorder or premelt clearly before the whole cluster melts. However, there seems not to be a considerable amount of diffusion out from the (100) faces. The 891 atom octahedron also seems to stay in the same structure until it melts and no marked rounding of the sharp corners happen below the melting temperature. This indicates that even if the octahedron

is not an energetically favoured structure (as compared to the Wulff polyhedron) it is anyway a stable structure which can not easily transform to a Wulff polyhedron or icosahedron at low temperatures.

#### 4. Conclusions

Using molecular dynamics with many-atom potentials we have shown that the melting temperature of copper clusters is roughly proportional to the average coordination number of atoms in the cluster and the reduction of the melting temperature is proportional to  $N^{-1/3}$ . The icosahedral clusters melt at slightly higher temperatures than the same size cubic structures. Large Wulff polyhedral and octahedral clusters retain their original structure until the melting temperature whereas small cubic clusters can transform to an other geometry already at low temperatures. Small cuboctahedra are not stable but transform to icosahedra.

#### References

- Martins, J., Buttet, J., Car, R.: Phys. Rev. B **31**, 1804 (1985).
- Bonačić-Koutecký, V., Fantucci, P., Koutecký, J.: Chem. Rev. **91**, 91 (1991).
- Manninen, M.: Phys. Rev. B **34**, 6886 (1986).
- Cleveland, C. L., Landman, U.: J. Chem. Phys. **94**, 7423 (1991).
- Raoult, B., Farges, F., De Feraudy, M. F., Torchet, G.: Z. Phys. D **12**, 85 (1989).
- Mansikka-aho, J., Manninen, M., Hammarén, E.: Z. Phys. D **21**, 271 (1991).
- Echt, O., Sattler, K., Recknagel, E.: Phys. Rev. Lett. **47**, 1121 (1981).
- Martin, T. P., Bergmann, T., Göhlich, H., Lange, T.: Chem. Phys. Lett. **176**, 343 (1991).
- Güvenc, Z. B., Jellinek, J.: In *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena, S. N. Khanna, B. K. Rao (Kluwer Academic Publ., Dordrecht 1992).
- Buffat, Ph., Borel, J-P.: Phys. Rev. A **13**, 2287 (1976).
- Ercolessi, F., Andreoni, W., Tosatti, E.: Phys. Rev. Lett. **66**, 911 (1991).
- Jacobsen, K., W., Nørskov, J. K., Puska, M. J.: Phys. Rev. B **35**, 7423 (1987).
- Häkkinen, H., Manninen, M.: J. Phys: Cond. Matt. **1**, 9765 (1989).
- Valkealahti, S., Manninen, M.: Comp. Mat. Sci. (submitted).
- Valkealahti, S., Manninen, M.: Phys. Rev. B **45**, 9459 (1992).
- Jellinek, J., Güvenc, Z. B.: In *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena, S. N. Khanna, B. K. Rao (Kluwer Academic Publ., Dordrecht 1992).
- Häkkinen, H., Manninen, M.: Phys. Rev. B **46**, 1725 (1992).