

Melting of Small Gold Particles: Mechanism and Size Effects

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(Received 23 August 1990)

We present extensive molecular-dynamics simulations of small gold particles of $N=100-900$ atoms. We use a many-body interatomic potential of proven accuracy for gold surfaces. Structural properties are determined with various annealing strategies. Our results provide for the first time a microscopic description of the melting transition of metal clusters, revealing in particular the formation of a liquid skin as precursor effect for $N > 350$. The experimentally observed sharp decrease of the melting temperature with decreasing size is recovered. Implications for larger sizes, as well as for other metals, are discussed.

PACS numbers: 64.70.Dv, 68.35.Bs, 82.65.Dp

A strong need exists for a microscopic description of the melting process of metal clusters, especially in view of the growing interest in their properties and applications. It has long been known that the melting temperature T_M decreases with decreasing diameter d .¹ Several phenomenological models, starting from that of Pawlow,² have been proposed to account for this fact. Almost all consider the cluster as consisting of “bulk” and “surface” atoms, and the drop of $T_M(d)$ results from the fact that, at the bulk melting temperature $T_M(\infty)$, the *surface* free energy of the liquid is lower than that of the crystal.

Although qualitatively correct, it is doubtful whether such simple approaches should remain quantitatively valid down to clusters with a number of atoms $N < 1000$. Here, surfaces are far from being ideal owing to the limited size of the facets—which may influence, e.g., the onset of surface reconstruction³—and to the large fraction of atoms on edges and vertices that may induce large relaxation effects.⁴ The assumption of a size-independent surface energy is therefore questionable, and the very concept of surface energy ill defined. Moreover, a possible “surface melting” stage⁵ is neglected and could instead play a role in the process.

So far, a microscopic description of melting has been attempted only for rare-gas clusters of relatively small sizes ($N < 200$).⁶ Experimentally, however, most of the work has been devoted to metal clusters and to sizes in the range $N \sim 100-1000$. Noble metals, and more particularly gold clusters, have recently been the object of several studies, which have shown the existence of isomers of different topologies⁷ as well as the strong effect of the supporting substrate.⁸ First-principles molecular-dynamics (MD) calculations in this size range are not within current capabilities, also in view of the fact that “long” simulation runs on a time scale of at least 10^{-10} s are needed. Therefore, one has to resort to empirical interaction models. For our investigation of Au_N clusters with $N > 100$, we have used the many-body “glue” Ham-

iltonian,⁹ which predicts $T_M(\infty)$ within 2% of experiment,¹⁰ and successfully describes the structure and energetics of the low-index reconstructed surfaces of Au as well as of the vicinals in considerable detail.⁹ We have used standard microcanonical MD, without boundary conditions (cluster in vacuum), with a time step $\Delta t = 7.14 \times 10^{-15}$ s. After determining the stable $T=0$ structures, we have studied the behavior upon heating. With increasing temperature, we find for the larger clusters studied (a) onset of surface diffusion, (b) formation of “liquid patches” at the surface, and (c) abrupt overall melting of the whole cluster. The smaller clusters, instead, melt without surface precursor effects.

Clearly, an exhaustive search for the minimum-energy structure¹¹ in this size region is out of question, owing to the inordinate increase in the number of nearly equivalent local-energy minima. This problem becomes acute in our case, owing to the well-known general tendency of Au surfaces to contract and become close packed. In particular, we find that high- T annealing often leads to ball-like glassy (g) clusters—whose variety is virtually unlimited—which are energetically close to (but not necessarily lower than) fully relaxed and carefully optimized crystalline (c) clusters. In fact, the energy required to destroy the internal crystalline order is partly compensated by the energetic gain of surface atoms, which in a g cluster are free to rearrange in a nearly optimal (111) monolayerlike packing. To overcome this problem, we have used a “surface annealing” strategy, whereby a given initial structure—chosen among the most likely ones—is first relaxed by a damped MD run. Subsequently, the internal atoms are frozen in this relaxed but still c - or quasi- c -structure and a high- T annealing is performed in which only surface atoms are allowed to move. Finally, all atoms are set free to move and relax to the nearest local minimum. This procedure allows extensive restructuring of surfaces, but prevents glassification. An important result is that the surface of c clusters needs to be “reconstructed”—or simply made

denser than a chunk of bulk material—before an optimal cluster is found.

For $200 < N < 900$, cuboctahedra are favored over D-Wulff polyhedra and icosahedra in this order. This result contrasts with Ino's prediction¹² of stable icosahedral gold particles for $N < 40\,000$ ($d < 107$ Å), based on macroscopic concepts. Experiments do not clearly indicate a preferred structure. Twinned particles (such as icosahedra) often appear,⁷ but single Au fcc crystals have also been observed by electron microscopy^{7,13} and x-ray-absorption spectroscopy.¹⁴ Structural energy differences are probably tiny and strongly dependent on temperature, impurities, and effect of the substrate. Moreover, the particles could be trapped in metastable states. For $N \sim 100$ –200, glassy clusters seem to be favored in our model (all the crystal-like structures investigated were found to be unstable), but are rarely observed. The discrepancy could be due to the stabilizing effect of the substrate.⁸ However, in this size range,^{11,15} the reliability of the potential also begins to be questionable.

For our melting investigation, we have chosen three cuboctahedra with $N=219$, 477, and 879. They all have tiny (100) facets with four atoms arranged in a 2×2 square, but the central atom in the 3×3 (100) plane underneath is missing, allowing the 2×2 square to subside into the hole and giving rise to a rather compact geometry. This structure gives a slight energetic advantage over normal cuboctahedra. For each cluster, we have performed MD runs of 5000 time steps (≈ 35 ps) at various energies far from the melting region, while at several points near T_M the systems were equilibrated for 40000 steps (≈ 280 ps), and data were collected in a further 40000-step run. The quantities we monitored are the internal energy $\epsilon(T)$ and the specific heat $C(T)$, the density distribution and the diffusion as a function of the radial distance R from the center of mass (c.m.), the structure factor $S(k)$ for k oriented along $\langle 110 \rangle$ directions, the average coordination number and contraction. While the behavior of the two latter quantities does not exhibit any discontinuities, the thermal variation of all the others provides a clear and consistent identification of the melting transition.

Typical signatures of melting obtained from the caloric curves (Fig. 1) are (i) a jump in $\epsilon(T)$, corresponding to the latent heat of fusion ΔH_M , which, however, tends to disappear as the cluster size is decreased, and (ii) an increase of $C(T)$ (the slope of the curves). This indicates $T_M \approx 500$, 820, and 980 K for $N=219$, 477, and 879, respectively, to be compared with $T_M(\infty) \approx 1350$ K of our model. Such values are consistent with the experimental results of Buffat and Borel for these sizes,¹⁶ and are significantly lower than those predicted by Pawlow's theory (850, 970, and 1040 K, using parameters from Ref. 16).

Interestingly, ΔH_M decreases steadily from 114 meV/

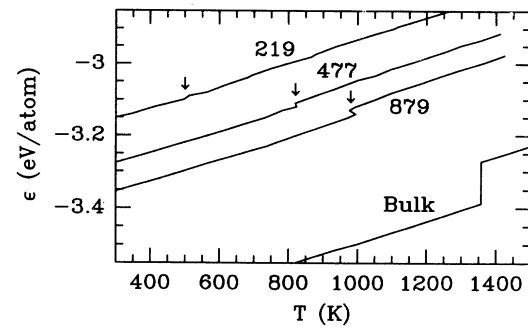


FIG. 1. Internal energy as a function of temperature for $N=219$, 477, and 879, and for the infinite bulk. The arrows indicate the estimated melting points.

atom (bulk) to 23 ($N=879$) and 10 ($N=477$). No discontinuity in the energy can be seen for $N=219$, consistent with the stability of g structures found for this size at $T=0$. Note that for a given N the typical energy difference between different structures at $T=0$ is ~ 10 meV/atom,¹¹ so that the decrease of ΔH_M with decreasing N is a genuine effect and not a consequence of dealing with nonoptimal structures. While the drop of T_M with size seems to suggest a critical diameter $d_c \sim 14$ Å ($N_c \sim 90$), where $T_M(d_c)=0$, ΔH_M drops faster and vanishes around $d^* \sim 21$ Å ($N^* \sim 300$). Therefore, for $d=d^*$ the entropy change on melting vanishes, while T_M is still finite. This is probably connected with the relatively ordered atomic arrangement of *all* surface atoms on the liquid surface of Au.¹⁷ For Lennard-Jones clusters, in fact, this behavior is not observed.⁶ Between d_c and d^* , melting then yields to a glass-liquid transition, signaled by the onset of diffusion. Therefore, our results for Au₂₁₉, which lie in this region, must be interpreted with some caution, since the initial c structure was probably metastable. In fact, the caloric curve obtained when starting from a *glassy* Au₂₁₉ is practically indistinguishable. The above estimate for d_c also determines a lower bound for the cluster size at which melting can still be defined in analogy with bulk melting.

Figure 2 shows the diffusion coefficient as a function of T for different spherical shells and the radial density distribution (referred to c.m.) for Au₈₇₉. At $T_M \approx 980$ K (Fig. 1), there is a sudden increase of diffusion for all the shells and a drastic structural change. For the two outermost shells, however, diffusion already reaches liquidlike values around a typical temperature $T_S \sim 800$ K.¹⁸ At T_S , the specific heat also increases slightly, and the radial density distribution changes near the surface, where it becomes similar to that of the liquid cluster, while retaining the c peaks in the inner part. Therefore, Fig. 2 unambiguously indicates that melting initiates at the surface. When T_M is reached, the liquid seed already present propagates to the whole cluster. In partic-

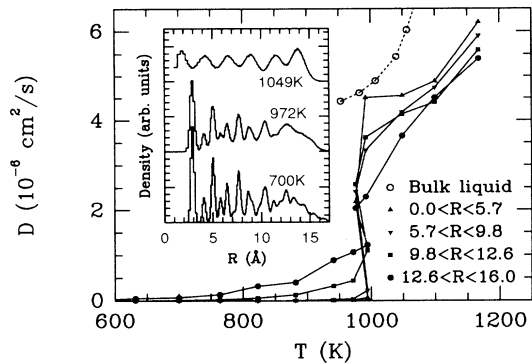


FIG. 2. Au_{879} : T dependence of the diffusion coefficient for different shells (see text), compared with that for the supercooled bulk liquid. Inset: Radial density distribution at $T=700, 972,$ and 1049 K.

ular, this makes overheating effects very modest, at least in our simulation. The diffusivity of surface atoms is strongly anisotropic. The ratio between the diffusion coefficients for atoms on the (100) and in the middle of the (111) facets is about 3 immediately below T_M , and increases strongly with decreasing T .

Au_{477} exhibits a very similar behavior, with $T_M \approx 820$ K and $T_S \sim 750$ K. While T_M is strongly dependent on the cluster size, T_S (which marks the onset of surface diffusion) depends only weakly on it, presumably through the variation of the fraction of edge and corner atoms relative to all surface atoms. As a result, the T window of the “surface melting regime” shrinks as the cluster size is decreased, and tends to disappear when the cluster is small enough to have $T_M < T_S$ (extrapolated). We estimate that this condition occurs when $T_M \sim 700\text{--}750$ K, i.e., $N \sim 300\text{--}350$. The smallest case studied, Au_{219} , indeed appears to melt as a whole near $T_M \approx 500$ K, without any appreciable increase of surface diffusion below T_M .

In order to facilitate comparison with the experiment in Ref. 16, we have also calculated the thermal dependence of the structure factor $S(220)$ and of its integral $I(T)$, i.e., the effective Debye-Waller factor (Fig. 3). For the two larger clusters, $\ln I(T)$ decreases nearly linearly with T up to T_S , indicating harmonic behavior. At higher T , surface diffusion sets in, and the increase of negative slope is clearly related to the progressive loss of crystalline order at the surfaces. Au_{219} , instead, is always very anharmonic, and quickly loses crystalline order on heating (but its diffusion coefficient remains low up to T_M). However, this could be due to instability against glassification as discussed above. Our results show clearly that the crystalline structure factor strongly depends on the size of the cluster, in contrast to the crude assumption made in simple models.¹⁶

What do these results suggest for larger sizes and other metals? Experiments on Pb (Refs. 19 and 20) show that flat surfaces become disordered below $T_M(\infty)$ (sur-

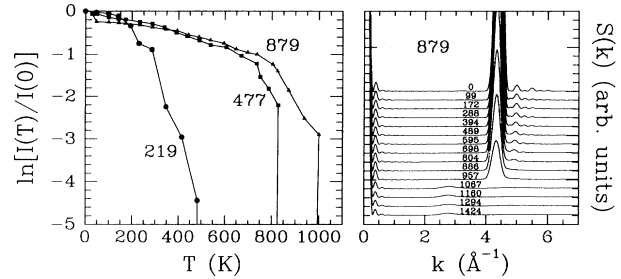


FIG. 3. Logarithm of the effective Debye-Waller factor as a function of T for Au_{219} , Au_{477} , and Au_{879} (left), and T dependence of $S(k)$, with k along the $\langle 110 \rangle$ direction, for Au_{879} (right).

face melting), with the notable exception of the (111) surface. $\text{Au}(111)$ is also crystalline at T_M , both experimentally²¹ and within the present model.¹⁰ Therefore, larger clusters could still exhibit liquidlike disorder on non-(111) facets and on edges, while (111) facets should remain essentially crystalline up to melting. Conversely, extended liquidlike areas on metal cluster surfaces should be impossible to observe in icosahedral structures, where only (111) facets are present. Since (111) has a lower surface free energy than the liquid surface at T_M ,²⁰ it would even seem possible to have a transition from cuboctahedra to icosahedra with increasing T . These general considerations could be of help in understanding the structural transformations that clusters undergo under electron-beam irradiation.⁷

In conclusion, we find cuboctahedral structures to be favored for small Au particles at $T=0$. However, energy differences with other structures are very small, and the nature of the optimal structure for a given material may strongly depend on the details of atomic interactions. In metals, surface energy anisotropy is believed to be smaller than in rare gases, thus increasing the stability of single crystals.

More generally, we have shown that in the size range $N \sim 100\text{--}1000$ (i) simple models for metal cluster melting constructed in the macroscopic limit are not suitable since surface effects play a crucial role, and (ii) a sharp melting transition can be clearly identified, in contrast to the behavior of clusters with 10–20 atoms.⁶ Moreover, (iii) the melting mechanism, here studied in detail for the first time, reveals the presence of precursor effects, such as increased diffusivity of atoms located at edges between facets and on facets (if present) exhibiting surface melting. The knowledge of high atomic diffusivity in metal particles is important for applications of heterogeneous catalysis.²² Premelting effects should be observable with accurate calorimetric measurements and other tools such as quasielastic scattering. Finally, we emphasize that in order to compare the results of our simulations to experiments—for both structural and thermal behavior—it would be highly desirable to have experi-

mental data on size-selected and “free” (unsupported) clusters.

Interest in this subject was stimulated by discussions with J.-P. Borel. We are also grateful to Ph. Buffat, M. Flüeli, M. Kappes, M. Parrinello, L. Pietronero, and J. Saenz for useful discussions and correspondence.

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