# Melting and nonmelting behavior of the Au(111) surface

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A molecular-dynamics study of the melting behavior of Au(111) (both reconstructed and unreconstructed) has been carried out using a recently developed many-body force scheme. The reconstructed (denser) surface remains stable up to the bulk melting temperature $T_M$, showing no form of microscopic surface melting. By contrast, the two outermost layers of the unreconstructed surface "melt" $\sim 100$ K below $T_M$. However, no more layers melt as $T_M$ is approached. The nonmelting of Au(111) is contrasted with the gradual melting behavior of Lennard-Jones surfaces.

The idea that crystal melting could be a surface-initiated process is very old,[1] and some evidence has been provided long ago by macroscopic means.[2] Recently, interest in surface melting has been revived by qualitative ideas,[3] as well as by newly available microscopic surface tools,[4] and by the possibility to realistically simulate the warm crystal surface on the computer. The best simulation so far is that of Lennard-Jones (LJ) crystal surfaces, thoroughly characterized by Allen, De Wette, and Rahman[5] and by Broughton and co-workers.[6] They show clear evidence of surface-nucleated melting, down to temperatures as low as $\frac{3}{4} T_M$, in remarkable agreement with predictions based on simple qualitative models.[3,7] Experimentally, surface-initiated melting has been recently demonstrated on Pb(110)[4] as well as on Ar.[8] For Pb(110), a close correlation has been found[9] between anharmonic surface outwards relaxation and the onset of surface disorder, as was predicted.[7] The general situation is however still far from clear. In the case of Lennard-Jones crystals, the role of vacancy-related surface roughness could be important, and is as yet unclear.[10] Moreover, the thermodynamics of the warm surface is not well established in that one does not know if surface melting is or is not a well-defined phase transition, and of what type. Finally, metals are most commonly used for microscopic experiments, but a LJ crystal is not a good description for them.

We have undertaken a series of molecular-dynamics (MD) calculations to characterize the melting behavior of the Au(111) surface. We have used the many-body force scheme ("glue" potential) introduced by Ercolessi, Parrinello, and Tosatti.[11-13] This potential, though classical, reproduces many features due in reality to the bandlike $d$ electrons. In particular, the Au surface reconstructions are modeled reasonably well by this potential. For the Au(111) surface, specifically, the many-body model predicts a distorted topmost (111) layer with higher densi-

ty,[14] in qualitative agreement with experiment.[15]

We have used a slab geometry, with the two bottom layers assumed to be rigid in their bulklike positions to mimic the contact with a semi-infinite bulk. Periodic boundary conditions are used along $x$ and $y$, and free motion is allowed along $z$ (zero pressure). In order to minimize spurious slab effects, the lateral box size was adjusted to match the mean lattice parameter at $T \sim 1350$ K, as extracted from an independent bulk simulation.[13] Atom evaporation is a very improbable event in this system, and we have observed none during our simulations. On the other hand, we have directly checked that a surface vacancy or adatom has an extremely short lifetime ($\sim 10^{-13}$ and $\sim 10^{-12}$ s, respectively) before being annealed out. Therefore, the reconstructed surface is free of vacancies and adatoms at almost any time. Hence, we argue that a solid-vacuum interface—such as that realized in our simulation—should behave very similarly to the equilibrium solid-vapor interface.[16] For most of the calculations we have used slabs of 40 layers with 56 particles on each layer. Our $(x,y)$ cell is defined by $L(a/2)(1,-1,0) \times M(a/2)(1,1,-2)$ with $L=7$ and $M=4$. In this approximately square cell, we can accommodate either an unreconstructed surface (56 top-layer atoms), or a denser unreconstructed surface (64 top-layer atoms). This corresponds to higher surface density $\delta\rho_s/\rho_s \sim 14\%$. This value is slightly higher than the value $\delta\rho_s/\rho_s \sim 9\%$, which is optimal for our potential,[14] but has the advantage of requiring a smaller size cell. The total number of particles with reconstruction is, therefore, $N = 56 \times 39 + 64 = 2248$, of which 112 belong to the rigid layers. This requires about 1 CPU second per MD step on an IBM 3090 with vector facility. Annealing of this system at low temperatures leads to an ordered surface structure, studied in detail elsewhere.[14] This reconstructed surface is, as it should be, much more stable and well packed than the corresponding unreconstructed surface.

To check for lateral size effects we have doubled, in some calculations, the lateral size in each direction (bringing in this way to 224 the number of particles of an unreconstructed layer), and decreased the number of layers to 12 (of which two are rigid) to limit the increase in the total number of particles. In these runs we have found no difference in behavior with the other runs, thus indicating that 56 particles per layer are sufficient for present purposes.

We have performed both microcanonical and canonical runs. Canonical runs have been realized by crudely rescaling the particles velocities at each time step to adjust the kinetic energy to conform to the desired temperature. Figure 1 summarizes the results of the canonical runs, for the reconstructed Au(111) surface, and presents the number $n$ of molten layers at each temperature. There are several qualitative ways to define a molten layer: (a) the intralayer pair correlations have lost their crystalline shell structure; (b) diffusion is linear with time and large; (c) the average energy per atom is $\sim 0.12$ eV larger than in a typical bulk layer; (d) the in-plane orientational (hexatic) order parameter $O_6$ has dropped from close to 1 to close to 0. We define $O_6 = |\sum_{ij}W_{ij}e^{6i\theta_{ij}}|/\sum_{ij}W_{ij}$, where the sums run over first-neighbor pairs and $\theta_{ij}$ is the angle which the $i-j$ bond, projected on the $xy$ plane, forms with the $x$ axis. The weight function $W_{ij} = \exp[-(z_i-z_j)^2/2\delta^2]$, $\delta = 0.59$ Å, has the purpose of filtering out all "noncoplanar" neighbors. Figure 2 exemplifies the behavior of $O_6$ and of the $(x,y)$-averaged atomic density for a sample with $n = 18 \pm 2$ molten layers and $\langle T \rangle = 1350$ K. As a practical criterion, we call "solid" a layer with $O_6 > \frac{3}{4}$. We have checked that this definition generally fits well with the other criteria (a), (b), and (c) above. In particular, diffusion sets in rather sharply for $O_6$ smaller than this value.

Returning to Fig. 1, each arrow $nn'$ represents a simulation, beginning with $n$ and ending with $n'$ molten layers. Initial configurations with any number $n$ of molten layers are easily generated by a high-temperature run ($T > 1600$ K) where, starting from an initially solid slab, $n$ grows
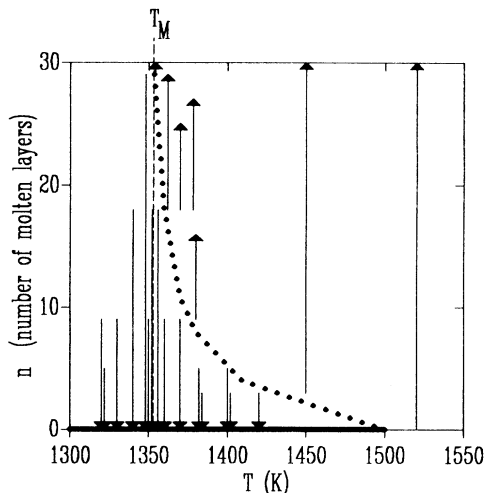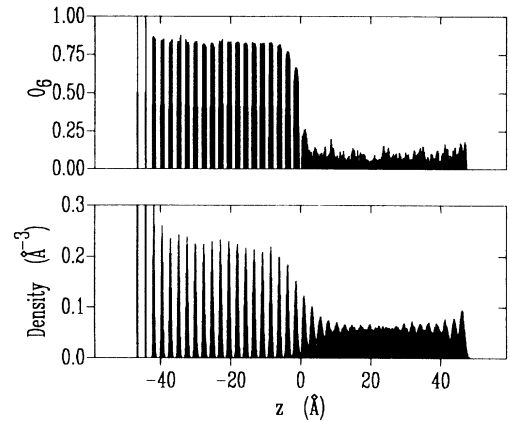


FIG. 2. Orientational order parameter $O_6$ and $(x,y)$-averaged density, for a microcanonical sample with $\langle n \rangle = 18$ molten layers and $\langle T \rangle = 1350$ K. The two leftmost layers are rigid. These data have been averaged over 2000 MD steps.

with time. Each run has typically required $\sim 10^4$ to $\sim 3 \times 10^5$ time steps, the larger times being required for runs close to the melting temperature. Since a time step $\Delta t = 7.14 \times 10^{-15}$ s has always been used, our equilibration times range from $\sim 10^{-10}$ s to $\sim 10^{-9}$ s. We generally find that the energy $E$ of a sample is rather accurately related to temperature and to $n$ by the simple relation $E = NC_VT + \Delta Hnn_L$ where $C_V = 3.1 \times 10^{-4}$ eV/(K atom) is the solid-bulk specific heat and $\Delta H = 0.12$ eV/atom is the bulk heat of melting for our model potential. Here $n_L$ is the number of particles in each layer. Up to a temperature $T_0 = 1357 \pm 5$ K, the only equilibrium configuration is crystalline ($n = 0$). Above $T_0$, we find two possibilities. If the initial liquid thickness is small enough, $n < v(T)$, the sample crystallizes, $n' = 0$. For $n > v(T)$, the sample melts completely, $n' \to \infty$ (really $n' \to 35$ due to our finite size and rigid layers). The "unstable line" $v(T)$ is oblique, and intersects zero at $T_1 \sim 1500$ K. Above $T_1$, any initial configuration, including $n = 0$, will melt.

We interpret the above as follows. The temperature $T_0$ is identified with the bulk melting (triple-point) temperature $T_M = T_0 = 1357 \pm 5$ K. This value is in fairly good agreement with the experimental value $T_M^{expt} = 1336$ K, confirming the good accuracy of the glue potential, also at high temperatures. The crystalline reconstructed surface is stable below $T_M$, and remains metastable between $T_M$ and $T_1$. Thus, microscopic surface melting does not occur on this surface. In principle, this does not imply that macroscopic surface melting, i.e., sudden formation of a thick liquid film extremely close to $T_M$, might not occur. We simply cannot address this question with our tools, due to size and time limitations. Within these limits, however, our surface is not only stable up to $T_M$, but can also sustain overheating by as much as $\sim 100$ K above $T_M$.

It is tempting to relate the lack of microscopic melting of the reconstructed Au(111) to its denser first-layer packing. To test this idea, and also to explore the more general possibility of a totally different behavior for a slightly different state of the surface, we have carried out



FIG. 1. Summary of the runs for the reconstructed Au(111) surface. The dotted line represents the curve of instability $v(T)$.

a parallel study of the unreconstructed surface. Here, the topmost layer is taken to be simply identical to all other layers, i.e., no extra atoms have been added. This state of the surface might be experimentally accessible, in spite of its substantially higher surface energy $\sigma$ (at $T=0$, $\sigma_{rec}=90.4$ meV/Å$^2$, $\sigma_{unrec}=96.6$ meV/Å$^2$).

Figure 3 describes our results for the unreconstructed Au(111) surface. Here, the first two layers melt simultaneously at $T^* \sim 1250$ K, with an energy increase $\Delta h \sim 0.03$ eV/atom, a value much lower than the bulk heat of melting. This may be due to the poor degree of packing of the unreconstructed surface layer and to the concurrent high quality of packing found on the double melted layer. This two-layer melting shows hysteresis, which could indicate a first-order character. Following this two-layer melting, one might have expected to observe the solid-liquid interface to propagate into the bulk, as $T_M$ is approached further. However, this does not happen, and the double-melted layer state remains stable up to $T_M$. Moreover, in analogy with the reconstructed surface, the two-layer state can be overheated for about $\sim 100$ K above $T_M$. We conclude that indeed a situation of poorer surface packing can bring about some microscopic surface melting. Yet, this "nucleus" does not propagate into the bulk to give rise to a thick liquid layer as $T_M$ is approached. In this sense, the lack of surface melting of Fig. 1 is confirmed.

We believe this nonmelting behavior to be an effect of the many-body forces. Specifically, the energetics of surface atoms, very poor in a system with two-body forces (such as LJ), becomes very much better once the many-body forces are included. For example, the (relative) excess energy of a surface atom with respect to a bulk atom at $T=0$, $(E_s-E_b)/|E_b|$, decreases from 0.29 for LJ(111) (Ref. 6) to 0.20 (ideal unrelaxed) to 0.17 (relaxed unreconstructed) to 0.13 [relaxed and reconstructed (111) surface]. As a consequence, all entropy-related quantities, such as thermal vibration and expansion, de-
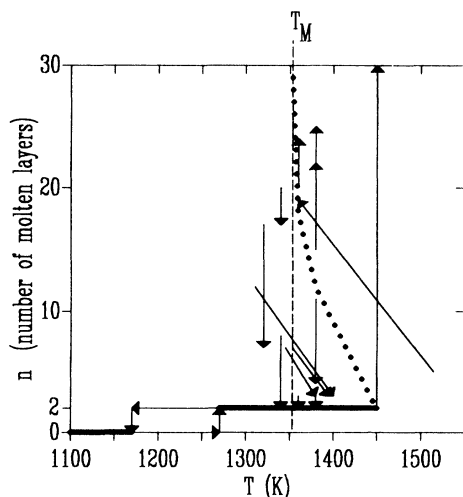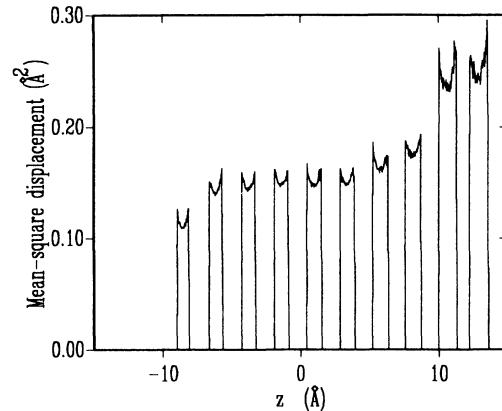


FIG. 4. Average-mean-square displacement $\langle u^2 \rangle$ (sum of the three components) as a function of $z$ for a reconstructed sample at $T=1350$ K, just below $T_M$. These data refer to a case with 12 layers, of which two are rigid. The decrease in $\langle u^2 \rangle$ for the leftmost layers is due to the contact with the rigid layers. The average $\langle u^2 \rangle$ for the surface (rightmost) layer is only $\sim 1.5$ times larger than in the bulk (see text).

fect concentration, etc., are expected to rise much higher near $T_M$ in a two-body system than in a many-body system. This particular point finds a direct confirmation by comparison of, e.g., the LJ(111) results of Broughton and Gilmer[6] with our Au(111) results. While the LJ surface is wobbly and full of defects already 5% below $T_M$, our reconstructed surface is still very much bulklike even at $T_M$. This point is particularly evident from the mean-square-vibration amplitudes of our reconstructed surface, shown in Fig. 4. Even as close to $T_M$ as 5 K, the surface is clearly still vibrationally stable, in contrast with the LJ case.[6] The mean-square first-layer vibration amplitude relative to the bulk for our reconstructed Au(111) surface is only 1.5 just below $T_M(T=1350$ K). The corresponding value for LJ(111) is already as high as 2 at $T/T_M=0.5$.[5]

Similar considerations also apply with respect to single models. In the Pietronero-Tosatti model the surface instability is caused precisely by the abnormal entropy-driven growth of surface thermal vibration and expansion. As shown by Jayanthi, Tosatti, and Pietronero,[7] even a small energetic strengthening—such as that caused by inwards relaxation—is very efficient in raising the vibrational surface instability and possibly eliminating surface melting. The conclusion to be drawn from these considerations is that the improved surface energetics of our metal as compared with, say a LJ crystal, implies a better surface stability against melting. The case of Au(111) is perhaps extreme, and surface stability is so strong as to completely prevent microscopic melting, allowing even the surface to be overheated, at least in the absence of surface steps.

In summary, we have shown the following. (a) A warm metal surface such as Au(111) behaves very differently from a LJ surface. (b) Microscopic surface melting does not occur (at least within a time scale of $10^{-9}$ s and with a temperature uncertainty of 5 K) on the well-packed reconstructed surface. (c) Melting of the first two layers



FIG. 3. Summary of the runs for the unreconstructed Au(111) surface. The dotted line represents the curve of instability $\nu(T)$.

does take place on a poorly packed surface, such as the unreconstructed Au(111); however, no more than two layers melt. (d) The "nonmolten" surfaces can be overheated for as much as 100 to 150 K above bulk melting. (e) The contrasting behavior of Au(111) and LJ(111) is plausibly related to the improved surface stability of the former, brought about by many-body forces.

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