Pergamon

DIFFERENT MELTING BEHAVIOR OF LEAD SURFACES

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By using our recently constructed many-body potential, the temperature-dependent structure and dynamics of lead surface are studied. The results on (100) surface are compared with that of the (110) and (111) surface. We find that, different from the non-melting behavior of the (111) surface and the melting behavior of (110) surface, the (100) surface is an incompleted melting surface. These results are in good agreement with the experimental data. The possible reason for the different behavior of these surfaces is also discussed.
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The understanding of the melting of a solid at the microscopic level is a long standing problem in condensed-matter physics. Recently, this problem is receiving renewed interest because new experimental evidence has shown the importance of the surface in the melting process. It is found that the melting is crystalline face dependent. Thus, while the (110) surface of some fcc metals (Cu, Al and Pb) exhibits surface melting, the close-packed (111) surface of these metals can preserve its crystalline order even above the bulk melting temperature, and fcc (100) surface shows the so-called incompleted surface melting, *i.e.*, the (100) surface becomes disorder in several outmost layers just under bulk melting point, however the 'melting front' does not propagate to the deeper layers as the temperature is close to the melting temperature. For lead, even 100K below the melting temperature, the outmost layer of (110) surface has become liquid-like, [1–13] however the (111) surface can even be overheated about 120K above the melting temperature, [13, 14] the incompleted melting behavior of the (100) surface has also observed. [13–17]

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The detailed theoretical consideration to the surface melting includes the thermodynamic methods based on Landau energy functional, [18–21] lattice-instability models [22] and the molecular dynamics (MD) simulation. Using many-body interaction potentials, the molecular dynamics simulation has been performed for some fcc metal (Au, Al, Cu, Ni and Pb) surfaces. [23–35] These investigations provided the evidence for the disordering of the (110) surface of fcc metals via a vacancy–adatom generation mechanism mediating the formation of an adatom layer. The (111) surface of fcc metal does not show any surface-melting behavior. However, to our knowledge, the theoretical study on (100) surface is very much limited, which is experimentally observed to be a incompleted melting surface.

To make a contribution to the understanding of the atomic-scale mechanism on surface melting, we have studied the thermal behavior of the (110), (100) and (111) surface of lead using MD simulation with our recent fitted potential, [36] which is numerically optimized from a large amount of physical quantities. This potential has been extensively tested and can correctly reproduce many basic properties of lead in crys-

talline and non-crystalline phases. Especially, the obtained surface energy and surface relaxation are in good agreement with the experimental results. The theoretical melting point is 590.0K±5.0K in agreement with the experimental value of 600.8K.

In present studies, the calculations are performed on the surface consisting of 30 layers, each layer contains 100, 88 and 100 atoms for (100), (110) and (111) surface respectively. The atoms in the bottom four layers keep rigid to mimic the semi-infinite solid, the rest are allowed to move. The periodic boundary conditions are imposed in the directions parallel to the surface. Slabs of this size have shown to be sufficiently thick and large for the reliable description of disorder and premelting phenomena for surface melting. The lattice constants are changed with temperature according to the expansion coefficient found in MD simulation under zero pressure. Our simulation uses standard constant-energy MD technique. The equations of motion are integrated using the Verlet method with time step of 3.6×10^{-15}s. At each temperature the system is allowed to propagate over at least 10^5 time steps to ensure thermal equilibration. At the temperature near the melting point, the length of the runs is much longer, i.e. up to 2×10^5 time steps.

To characterize the structural change of the surfaces, we calculate the two-dimensional pair correlation function $g(r)$,

$$g(r) = \langle \frac{1}{n_l} \sum_{i,j \in l}' \frac{1}{2\pi r} \delta(r_{ij,||} - r) \rangle, \tag{1}$$

where $r_{ij,||}$ is the magnitude of the component of $\mathbf{r}_i - \mathbf{r}_j$ parallel to the surface, n_l is the instantaneous number of atoms in layer l, and angular brackets denote averaging over time.

The square of structure factor is usually used as an order parameter, the square of structure factor of the *lth* layer is

$$|S(\mathbf{k})|^2 = |\langle \frac{1}{n_l} \sum_{i \in l} exp(i\mathbf{k} \cdot \mathbf{r}_i)|\rangle^2, \tag{2}$$

where $\mathbf{k}$ is the reciprocal-lattice vector parallel to the surface and the sum runs over the position vectors $\mathbf{r_i}$ of the atom i in the layer l. In this paper, we choose $\mathbf{k} = (\frac{2\pi}{a}, \frac{2\sqrt{2}\pi}{a}, 0)$, $\mathbf{k} = (\frac{2\sqrt{2}\pi}{a}, \frac{2\sqrt{2}\pi}{a}, 0)$ for (110) and (100) surface respectively, where a is the lattice constant. The unity of the structure factor indicates a perfect order solid, being zero of the structure factor refers to the disorder.

Our calculations clearly show that (111) surface is a non-melting surface. Fig. 1 is the density profiles for the (111) surface at the melting temperature, where the
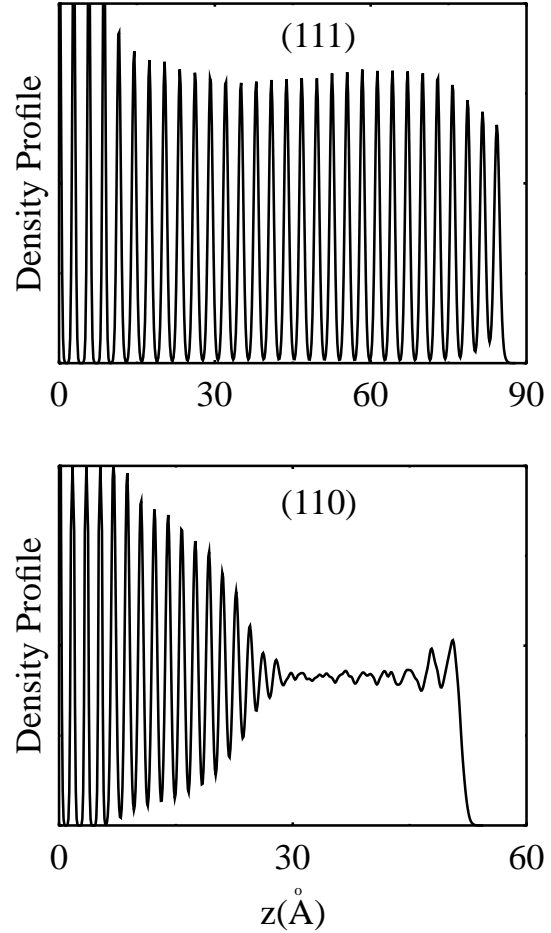

Fig. 1. The density profiles of the lead (111) surface (upper panel) and (110) surface (lower panel) at melting temperature. The maxima in the density profile correspond to the layer positions of solid part. It clearly shows that the (111) surface is a non-melting surface in contrast to the (110) surface of melting.

maxima correspond to the layer position in the solid. It is clear that, for (111) surface, the solid-like layered structure is preserved up to the bulk melting temperature. Visual observation shows that the (111) surface indeed maintains its crystalline order at melting temperature after running 5 ns, even can be overheated, which is in agreement with the experimental observation. [13, 14]

The (110) surface displays surface-melting, in agreement with the experimental results the liquid-like layer is formed above 500K. Figure 2 shows the temperature dependence of the square of structure factor for the outmost six layers of (110) and (100) surface. We find that, at temperature below 300K the motion of atoms is mainly due to the lattice vibrations, the order parameter for the outmost layers of (110) surface remains large. Above 300K, a sharp change of $|S(\mathbf{k})|^2$ for the two outmost layers indicates the on-
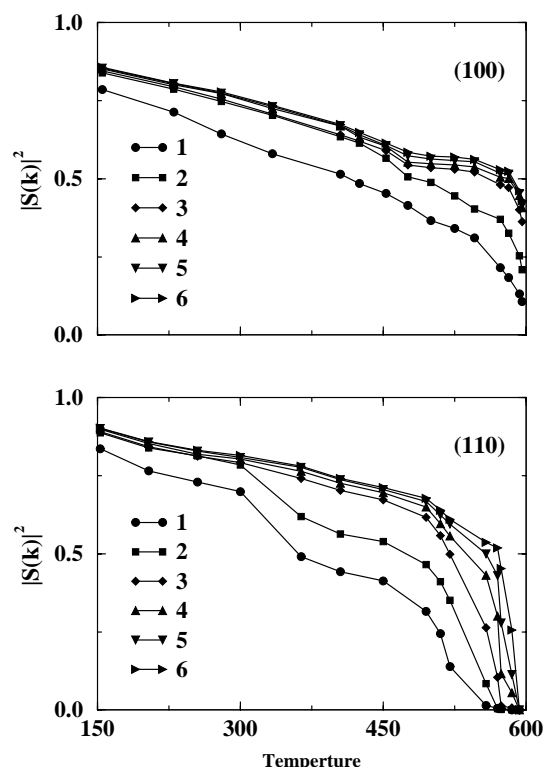
Fig. 2. Square of layer-structure factors, $|S(g)|^2$, as a function of temperature for the outmost six atomic layers of (110) surface (upper panel) and (100) surface (lower panel). For (110) surface, that $|S(g)|^2$ becomes zero above 500K implies the liquid-like formed; for (100) surface, except for the outmost two atomic layers, the preservation of crystalline order is a signature of incompleted surface melting near melting temperature, which are in agreement with the experimental results.
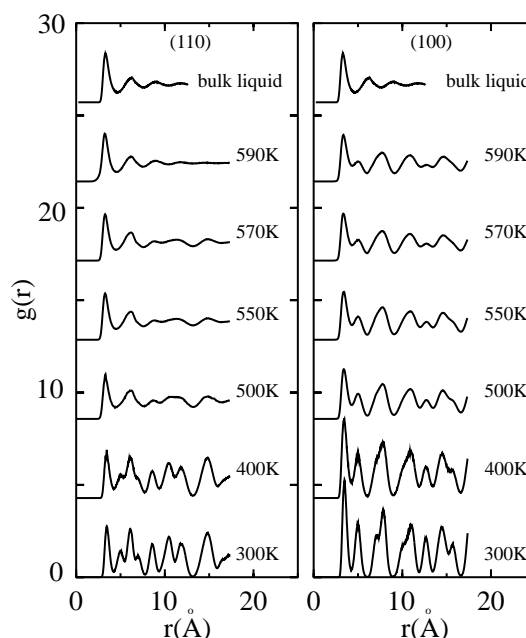

Fig. 3. The two-dimensional pair correlation function $g(r)$ for the first layer of (110) surface (left panel) and (100) surface (right panel) at different temperature. For (110) surface, above 500K, the first layer begins to lose the long rang order, and gradually becomes bulk-liquid like. For (100) surface, $g(r)$ changes gradually, to the melting temperature, the main feature of $g(r)$ remains.

set of vacancy–adatom pair. Being zero of $|S(\mathbf{k})|^2$ of the first layer above 520K implies that the first layer has lost its crystalline order and becomes a liquid-like layer, which is consistent with the experimental results that a liquid-like layer starts to form at this temperature. The change of the order parameter for the inner layers shows a similar trend with the first layer, which indicates the surface melting of (110) surface is layer-by-layer. The surface melting behavior of (110) surface can also be seen from the change of g(r), pair correlation function (Fig. 3). Above 500K, the first layer begins to lose the long rang order, and gradually becomes the bulk liquid-like. At 590K, g(r) of the outmost layer has the similar character as the bulk liquid. The density profiles at the melting temperature (Fig. 1) are another signature for the surface melting of (110) surface. At the melting temperature, several outmost layers have become liquid-like in contrast with the non-melting surface of (111) surface.

We find that, (100) surface displays incompleted

melting in consistent with the experimental results. From Fig. 2, we can see that the order parameter for the outmost atomic layers of (100) surface remains practically large up to 550K. Above 550K, the order parameter of the two outmost layers begins to sharply decreasing. However, the deeper layers does not show the behavior of the two outmost layers as the melting temperature is approached, the number of the disorder layers do not increase near the melting temperature. Figure 4 shows atomic positions near the bulk melting point for about 1 ns. The disorder is only observable on the two outmost layers, the crystalline order of inner layers is kept. This is a signature of incompleted surface melting. From Fig. 3, we can observe that, g(r) of outmost layer of (100) surface gradually changes, however as the melting point is approached, the main feature of g(r) remains unchanged, which could be attributed to the effect of crystalline order of the under-layers.

It is well known that the surface melting behavior could be quantitatively explained in terms of the interfacial free energies of the solid–vapor, solid–liquid, and liquid–vapor interface. However the exact calculation of the free energy is very difficult. The difference of melting behavior between the three studied
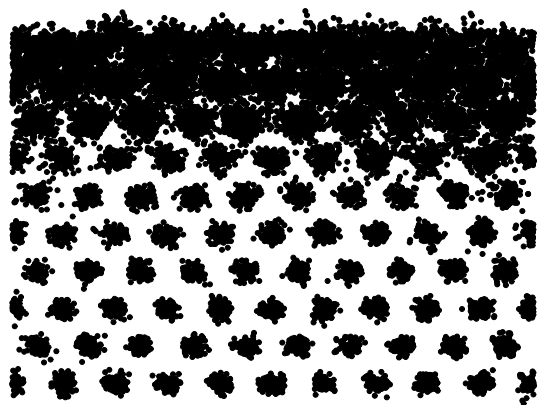
Fig. 4. Atomic positions near the bulk melting point for (100) surface for about 1.0 ns. The liquid layer of (100) surface is observable only on the outmost two layers.

surfaces can be understood from the energy and the structure point of view. First, as the main part of free energy, the surface energy may be an important factor in determining the melting behavior of surfaces, it is easy to understand the lower the surface energy, the higher the stability. The non-melting (111) surface has the lowest surface energy, the melting (110) surface has the highest surface energy, while the surface energy of (100) surface is in between, which displays incompleted melting. Secondly, the structural similarity between the surface and liquid may be another factor to affect the surface melting. The similarity can be seen from Fig. 3, where the structure of (110) surface is closer to the structure of liquid than that of (100) surface, which can make the (110) surface liquid-like without much rearrangement of atomic positions. It needs to point that, there may be other factors to affect the surface melting.

In summary, by using a realistic many-body potential, we have presented a first MD simulation on the (100) surface of lead, and compared its melting behavior with that of (100) and (111) surface. Our results show that, the (111) surface does not show any evidence of surface melting, and can even be overheated; the (110) surface begins to melting about 100K below the melting point. In contrast to the melting behavior of (110) surface and non-melting behavior of (111) surface, we find that, for the (100) surface, just two outmost layers seems to be melt about 50K below the melting temperature, however the 'melting front' does not propagate to the third and deeper layers as the melting temperature is approached. The possible reason for the different behavior of these surfaces is also observed. The obtained results are in good agreement with the experimental data, which also implies that the present potential can well describe the high temperature properties of lead surfaces.

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