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Molecular dynamics study of disordering, roughening, and premelting of the Pb(110) surface

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Abstract

Molecular dynamics simulations incorporating a many-body (glue) potential have been used to investigate the atomic structure and dynamics of the Pb(110) surface in the range from room temperature up to the bulk melting point. The surface region of Pb(110) begins to disorder approximately at 320 K, via the generation of vacancies and the formation of an adlayer. At about 400 K, adatoms begin to form so-called 'local steps' (small clusters of 2–3 atoms). The proliferation of atomic steps is observed above 400 K. Above 450 K, adatoms begin to collect in 'large' clusters (10–20 atoms), that can be associated with the beginning of the roughening transition. The anisotropic six-vertex model has been used to calculate a roughening transition temperature of $T_R^{6V} \approx 436$ K. The onset of a quasiliquid surface region is observed around a wetting temperature of $T_0 \approx 520$ K. The calculated values of the roughening transition temperature as well as the wetting temperature are in a good agreement with recent high-resolution low-energy diffraction measurements.

1. Introduction

Over the past ten years, a variety of experimental techniques (see Refs. [1,2] for details) have been used to study the Pb(110) surface, where both roughening and premelting (or wetting) transitions take place [3,4]. Since the first surface melting studies [3], which used medium energy ion scattering (MEIS), this surface has been the most widely investigated experimentally for surface melting phenomena. The Pb(110) surface may be regarded as the archetype for surface melting due to the following reasons: it tends to remain free of contamination in ultrahigh vacuum for long times, even at the high temperatures, and it is easy to control and monitor the Pb crystal close to the melting point, $T_m^{exp} = 600.7$ K, because of its low value.

Surface roughening and premelting are different disordering phenomena. On the roughened surface, atoms continue to occupy sites of the crystal lattice even though the surface width diverges on an atomic scale. In contrast, surface premelting may be distinguished from roughening by a lack of registry of the atoms in the premelted surface region with respect to the underlying crystal, which results in liquid-like properties of the surface region.

Despite the large amount of experimental information about the roughening and premelting of the Pb(110) surface, only limited effort has been devoted to the computer modeling of these phenomena on that surface. One successful approach has employed

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the so-called 'glue' potential [1,2], and has yielded results on disordering and premelting of that surface that are in good agreement with recent MEIS [5,6] and high-resolution low-energy electron-diffraction (HRLEED) [7] measurements.

In the present work, we briefly discuss the main results on the premelting of the Pb(110) surface, originally reported in Ref. [2], and present novel results on the theoretical estimation of the roughening transition temperature.

2. Simulation approach

In our molecular dynamics simulations [2] we used a semi-infinite system modeled via a slab of interacting dynamic atoms which, in addition, inter-

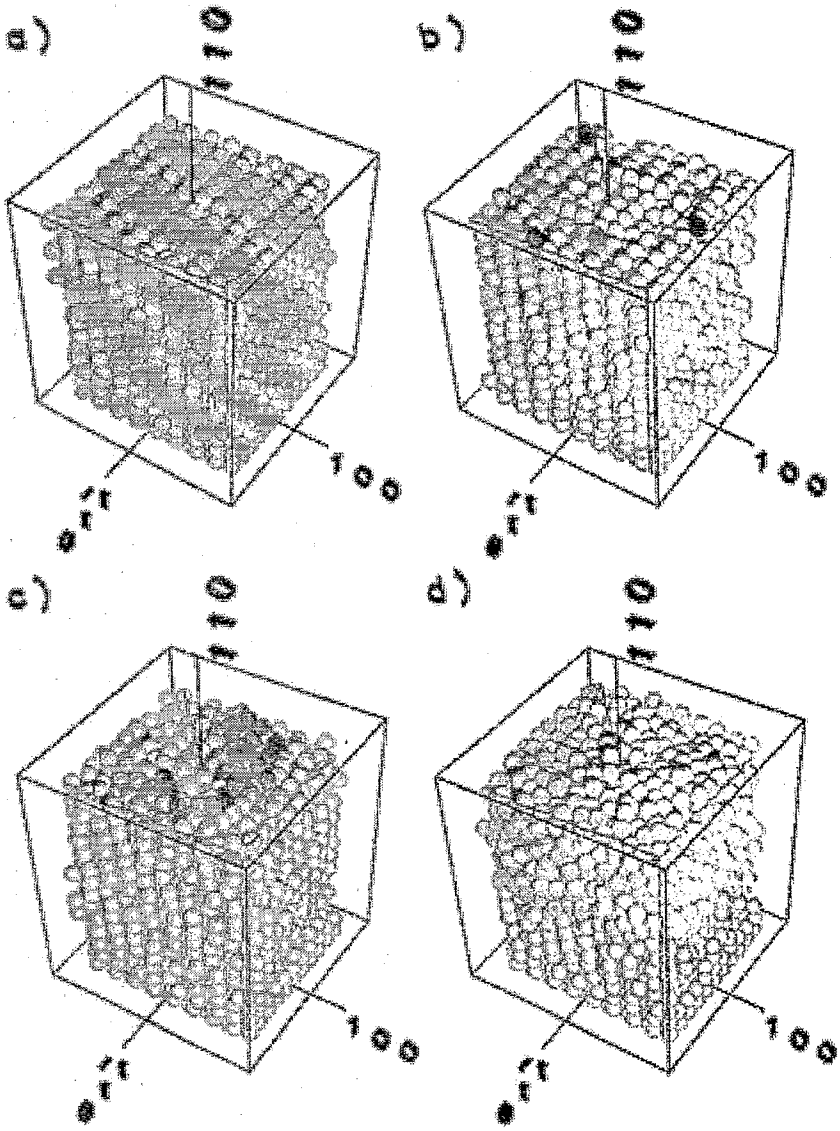

Fig. 1. Snapshots of the (110) slab at (a) $T = 300$ K, (b) $T = 400$ K, (c) $T = 460$ K and (d) $T = 620$ K. Adatoms (melted layers) are colored dark (light) gray.

act with a few layers of a static substrate of fcc (110) geometry (see Fig. 1). The interactions between atoms were described by the so-called many-body glue potential. The system consisted of 26 layers of 88 dynamic atoms each (8×11 atoms in the [001] and [$1\bar{1}0$] directions, respectively) on top of four static layers, resulting in 2288 dynamic atoms (2640 in total). The lattice constant of the static substrate at each temperature studied was adjusted to the value obtained from independent zero-pressure simulations of bulk Pb.

In the first stage of the study, we investigated the equilibrium properties of the (110) solid-melt and melt-vacuum interfaces at the coexistence temperature, $T_m^{GM} = 619 \pm 5$ K, which we interpreted to be the bulk melting point of Pb given by the glue model. In the second stage of the study, we performed systematic simulations in the range from room temperature up to the estimated bulk melting point to investigate the surface properties of the (110) slab.

3. Results and discussion

3.1. Surface premelting and equilibrium interphase interfaces

The calculated wetting temperature (T_0) of the Pb(110) surface was reported to be ~ 500 and ~ 520 K in Refs. [1,2], respectively. These results are in a good agreement with recent HRLEED measurements [7]. As was shown in Ref. [2], the thickness of the interfacial quasiliquid film grows logarithmically for $T > 520$ K with a correlation length of 7.7 Å, in close agreement with experimental results (6.3 Å [5]). We have also observed a strong tendency to densification and intralayer ordering of the two outermost liquid surface layers. This can be clearly seen from Fig. 1(d), which shows a snapshot of the (110) surface just above the estimated melting point. As was mentioned in [2], the dynamic structure of the solid–liquid interface exhibits fluctuating atomic-scale (111) facets.

3.2. Surface disordering and roughening

The Pb(110) surface begins to disorder via the generation of vacancies and the formation of an adlayer in the temperature range 320 K $< T <$ 360 K. As can been seen from Fig. 1(b), the adatoms are isolated from each other at $T = 400$ K. Just above 400 K adatoms begin to form 'small' clusters (2–3 atoms) or (following the terminology of paper [7]) so-called 'local steps'. The proliferation of atomic steps is observed at temperatures above 400 K. At about 450 K, adatoms begin to collect in 'large' clusters (10–20 atoms) (see Fig. 1(c)). We identify this type of surface behavior with the roughening transition. With further increases in temperature, the Pb (110) surface disorders by step formation, first along the [$1\bar{1}0$] direction and then along [001] direction.

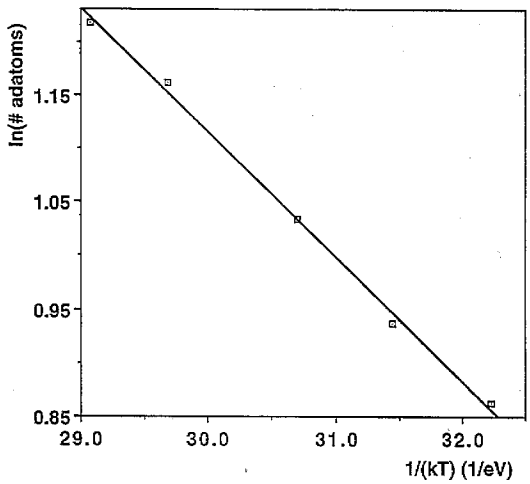

Fig. 2. The natural logarithm of the average number of adatoms vs. $(k_B T)^{-1}$.

In Fig. 2 we plot the logarithm of the average number of adatoms versus $(k_B T)^{-1}$ for 360 K $< T <$ 400 K. Within this temperature interval, all the atoms in the adlayer originate from the outermost surface layer. Using the slope of this data, we have estimated a vacancy–adatom formation energy ($E_{av} \sim 0.116$ eV). This value is very close to the analogous one ($E_{av} \sim 0.098$ eV), calculated for the ground state ($T = 0$ K) as the difference between the energy of the imperfect solid (containing one adatom and one vacancy at the surface, separated by a distance that prevents their interaction) and the energy of the perfect solid. It is instructive to note that this value is much smaller than those estimated in a similar manner in the investigations of the Cu(110) (~ 0.4 eV)

and Ni(110) (~ 1.0 eV) surfaces [8–10]. The vacancy–adatom formation energy is an important parameter which will be used in the next section in the calculation of the roughening transition temperature.

3.3. Calculation of the roughening transition temperature

We have mapped the solid–gas interface to an anisotropic six-vertex solid-on-solid (or the body-centered solid-on-solid (BCSOS)) model [7,11,12]. The exact transition temperature (T_R^{6V}) in the thermodynamic limit of the six-vertex model is given by

$$\Delta(T_R^{6V}) = -1, \tag{1}$$

with

$$\Delta(T) = \frac{A^2 + B^2 - 1}{2AB}, \tag{2}$$

where

$$A = \exp\left(-\frac{J_y}{k_B T}\right), \quad B = \exp\left(-\frac{J_x}{k_B T}\right). \tag{3}$$

J_y and J_x are the nearest neighbor and the next nearest neighbor coupling constants, respectively (i.e., the energy cost of broken bonds in the $[1\bar{1}0]$ and [001] directions). These energy parameters are determined from the surface excitation energies of the glue model. Fig. 3 shows the energy of an atom in the glue model lattice gas simulations, $E(C_1, C_2)$, where C_j is the number of the jth neighbors of an atom in the lattice. The energy costs of broken bonds (J_y and J_x) are found from the energy function $E = E(C_1, C_2)$ for a coordination corresponding to the outermost atom layer for which $C_1 = 7$ and $C_2 = 4$. As can be seen from Fig. 3,

$$J_y = E(7, 4) - E(6, 4) \tag{4}$$

is the derivative of $E(C_1, C_2)$ with respect to C_1.

$$J_x = E(7, 4) - E(7, 3) \tag{5}$$

is the distance between the $E(C_1, C_2)$ curves.

The calculated anisotropy ratio, $J_y : J_x = 3.23$, is close to the value of 3.46, which was extracted from HRLEED experiments [7]. The calculated vertex energies were then scaled so as to reproduce the correct energy for an adatom–vacancy pair (~ 0.116 eV). In this way we find: $J_y = 0.0444$ eV and $J_x = 0.0137$ eV. Using these energy parameters, the roughening temperature given by the glue potential six-vertex model is $T_R^{6V} \approx 436$ K $\approx 0.7\ T_m^{GM}$. Recent HRLEED measurements [7] detected the Pb(110) surface roughening transition at $T_R^{exp} = 415$ K $= 0.692\ T_m^{exp}$. It is interesting that both the theoretical and the experimental results for Pb are in a good agreement with earlier calculations for roughening of the fcc (110) surface of Lennard–Jones argon [13], which showed a roughening transition at $T_R = 0.7\ T_m$. The roughening transition temperature calculated in this manner also agrees fairly well with the development of adatom clusters on the Pb(110) surface in the molecular dynamics simulations.

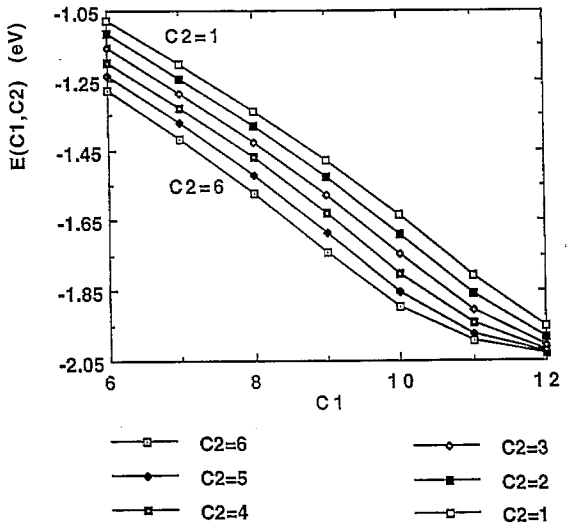

Fig. 3. Energy of an atom in the glue model lattice gas simulations vs. the number of jth neighbors for an atom in the lattice.

4. Conclusions

We have investigated disordering, roughening, and premelting of the Pb(110) surface, as well as the properties of the (110) solid–liquid interface at the coexistence temperature, by means of molecular dynamics simulations in which the glue model is used to describe many-body interactions. The results of these calculations are in a good agreement with available experimental data.

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