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Disordering and H-embrittlement of Pb(110)* surface using Embedded Atom Method and Molecular Dynamics

Prepared by:
Majid Karimi, PhD
Academic Rank:
Associate Professor
Institution:
Alabama A&M University
Physics Department

NASA/MSFC:
EH22
Office:
Metallic Materials
Division:
Metallurgical & Failure Analysis
Branch:

MSFC Colleague:
Ilmars Dalins, PhD
Contract No.:
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Problem statement

The dynamics and structure of crystal-melt interface are of great importance in crystal growth, melting, and other properties of solid liquid interface. The EAM, a semiempirical method developed by Daw and Baskes(1-3), for determining the energetics of atoms in a bulk environment, is a useful method for use in the computer simulation. The EAM functions of Pb in conjunction with the MD code are employed to study melting and disordering of Pb(100) surface. The EAM functions are fitted to the bulk experimental data at zero temperature and it is not clear if it will behave correctly at higher temperatures. In fact, it was shown(4) that use of a similar type of potential at higher temperatures might result in a negative coefficient of thermal expansion. The primary purpose of this report is to perform MD simulation combined with the EAM functions of lead to study melting of Pb(110) surface. This provide an accurate test of the EAM functions at higher temperatures. In particular, we calculate two dimensional structure factor, two dimensional pair distribution function, and density profile as a function of temperature up to the melting point of lead.

Methodology

Empirical pair potentials are suffering from two major problems, zero Cauchy pressure, i.e., \( P_{0} \neq 0 \) and equality of the vacancy formation energy \( E_{v} \) with the cohesive energy \( E_{c} \). In fact, in most of the metals \( P_{c} = 0 \) and \( E_{v} = E_{c} \). To overcome these shortcomings the EAM functions were developed. In the EAM, the energy of an assembly of atoms is calculated as a function of their atomic coordinates. The major contribution to the energy of each atom comes from the embedding term \( F \) which can be interpreted as the energy that is gained when an atom is embedded into the charge density created by all the other atoms. Embedding function is supplemented by a two body potential \( \phi \) mimicking the core-core repulsion,

\[
E_{i} = F_{i} + \sum_{j \neq i} \phi_{ij}(r_{ij}), \tag{1}
\]

where \( E_{i} \) is the energy of atom \( i \), \( F_{i} \) is the embedding energy of atom \( i \), \( \rho \) is the charge density at site \( i \), \( \phi_{ij} \) is the electrostatic interaction between cores of atoms \( i \) and \( j \), and \( r_{ij} \) is the interatomic distance between atoms \( i \) and \( j \). \( \rho \) is approximated by the superposition of atomic charge densities of all the other sites except site \( i \),

\[
\rho_{i} = \sum_{j \neq i} \rho_{j}^{a}, \tag{2}
\]

where \( \rho^{a} \) is the atomic charge density.
F and Φ are determined by considering functional forms for them and fitting them to the bulk properties of solid. The exponential forms were considered for p and Φ(2). Parameters of the EAM functions of lead are tabulated in Ref. (3). Conditions under which simulations were performed are reported in table (1), where T is the temperature, and tₑ and tₖ are equilibrium and total simulation times.

In the MD simulation, one simply integrates the classical equations of motion from which velocity and position of the N particles in the system of volume V are calculated. Energy E remains constant in a microcanonical ensemble, so the time average of any property is equal to the time average over a microcanonical ensemble of configurations each having that same E, V, and N(ergodicity)(5). Averages over a canonical ensemble, where V, T, and N are constant or over an isothermal-isobaric ensemble, where T, P, and N are constant are more easily compared with the experimental results than averages over a microcanonical ensemble. Algorithms for T and P control have already been developed. Calculation of interparticle forces usually accounts for about 85% of the total simulation time. If all particles interact, calculation of the forces require N(N-1)/2 calls to the force routine. However, calls to the force routine can be reduced to N×Nₖ if force is cut off beyond Nₖ neighbor of each atom.

We now briefly discuss the effects of hydrogen on metal-metal bonding using pair potential as well as the EAM and then compare our results. The interaction of the two metal atoms using the pair potential approach is,

\[ E_1 = \Phi_{M-M}(r_{M-M}) \]

where \( r_{M-M} \) is the interatomic distance. The force experienced by each atom is given by,

\[ F_1 = \Phi'_{M-M}(r_{M-M}) \]

We now put a hydrogen atom near to one of the metal atoms and calculate the potential and force between the two metal atoms;

\[ E_2 = \Phi_{M-M}(r_{M-M}) + \Phi_{H-M}(r_{H-M}) \]
\[ F_2 = \Phi'_{M-M}(r_{M-M}) \]

Therefore, in the pair potential approach, presence of the hydrogen does not change the force between the metal atoms. We now repeat the same calculation using the EAM formalism.

\[ E_1 = 2F_{M}( p_{M}(r_{M-M}) ) + \Phi_{H-M}(r_{H-M}) \]
\[ F_1 = 2F'_{M}( p_{M}(r_{M-M}) ) + \Phi'_{H-M}(r_{H-M}) \]
\[ E_z = F_H(\rho_H(r_H-M)) + F_H(\rho_H(r_H-M)) + \phi_H(\rho_H(r_H-M)) + \phi_H(\rho_H(r_H-M)), \]  
(9)

\[ F_2 = F'_H(\rho_H + \rho_H)\rho_H(r_H-M) + F'_H(\rho_H)\rho_H(r_H-M) + \phi'_H(\rho_H(r_H-M)), \]  
(10)

\[ F_2 - F_1 = F'_H(\rho_H + \rho_H)\rho_H(r_H-M) - F'_H(\rho_H)\rho_H(r_H-M). \]  
(11)

Assuming \( \rho_H \ll \rho_H \) (which is a reasonable approximation), we can Taylor expand \( F_2 - F_1 \),

\[ F_2 - F_1 = F''_H(\rho_H)\rho_H(\rho_H(r_H-M)), \]  
(12)

where \( F''_H > 0, \rho_H > 0, \) and \( \rho'_H < 0 \). This means that presence of the hydrogen will weaken the metal-metal bonding.

Results

a) Density profile \( \rho(z) \)

The atom density per unit length is:

\[ \rho(z) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left[-(z-z_0)^2/(2\sigma^2)\right] \]

where \( \sigma = 0.1 \) is the width parameter of the distribution, \( d_{110} = a/2\sqrt{2} \), and \( a = 4.91 \text{ Å} \). Result of the density profiles as a function of temperature is shown in Fig.(1).

b) Structure factor \( S_1(T) \)

The time-averaged squared modulus of the two dimensional structure factor for layer 1 at temperature \( T \) is:

\[ \langle S_1^2 \rangle = \frac{1}{n_1} \sum_i \exp[-ig.r_i^2], \]

where \( \langle \rangle \) denotes the time averaging, \( n_1 \) is the number of atoms in layer 1, and the sum is over the atoms of layer 1. \( \langle S_1^2 \rangle \) is calculated for \( g = 2\pi/a(1,0) \). Our result for \( \langle S_1^2 \rangle \) as a function of temperature \( T \) for the top nine layers are shown in Fig.(2).

Conclusions

The maximum in \( \rho(z) \) for layer L2 is lower than for L1 at temperatures 300 K and 400 K. A transfer of atoms between L2 to L1 occurs between 400 K to 500 K. Above 500 K an adatom is formed above L1 and leaves vacancies in L1 and L2. \( \langle S_1^2 \rangle \) versus \( T \) curves show disordering of the top two layers begins near 400 K. The number of adatoms increases with the temperature and is maximum near the bulk melting temperature.

Hydrogen embrittles the metal provided that the EAM approach is used for the energetics of the atoms. More work is needed to quantify the embrittlement near the grain boundaries in metals with and without the presence of hydrogen.
References

Because of the limited time available during the summer faculty program, we decided to first test our model predictions against a system with known experimental data. Pb was chosen partly because of availability of the EAM functions from our previous work and a rich collection of experimental data. Reference (6) has clearly shown that this type of calculation can easily be extended to the materials more relevant to the aerospace industry. Unfortunately, we did not have time to develop the EAM functions for that system.