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

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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 enviroment , 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., $P_c \neq 0$ 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 interpretted 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 Φ mimicing the core-core repulsion,

$$E_i = F_i + .5 \sum_{j \neq i} \Phi_{ij}(r_{ij}) \ , \tag{1}$$

where E_i is the energy of atom i, F_i is the embedding energy of atom
i, ρ is the charge density at site i, Φ_{ij} is the electrostatic
interaction between cores of atoms i and j, and r_{ij} is the
interatomic distance between atoms i and j. ρ 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   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 ρ and $\Phi(2)$. 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 t_E and t_T 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 $N*N_n$ if force is cut off beyond N_n 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,

$$E_1 = \Phi_{M-M}(r_{M-M}),\qquad\qquad (3)$$

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

$$F_1 = \Phi'_{M-M}(r_{M-M}).\qquad\qquad (4)$$

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

$$E_2 = \Phi_{M-M}(r_{M-M}) + \Phi_{H-M}(r_{H-M}),\qquad\qquad (5)$$

$$F_2 = \Phi'_{M-M}(r_{M-M}).\qquad\qquad (6)$$

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.

$$E_1 = 2F_M(\rho_M(r_{M-M})) + \Phi_{M-M}(r_{M-M}),\qquad\qquad (7)$$

$$F_1 = 2F'_M(\rho_M)\rho'_M(r_{M-M}) + \Phi'_{M-M}(r_{M-M}),\qquad\qquad (8)$$

$$E_2 = F_M(\rho_M(r_{M-M}) + \rho_H(r_{H-M})) + F_M(\rho_M(r_{M-M})) + F_H(\rho_M(r_{H-M})) +$$

$$\Phi_{M-M}(r_{M-M}) + \Phi_{H-M}(r_{H-M}), \qquad (9)$$

$$F_2 = F_M'(\rho_M + \rho_H)\rho_M'(r_{M-M}) + F_M'(\rho_M)\rho_M'(r_{M-M}) + \Phi_{M-M}'(r_{M-M}), \qquad (10)$$

$$F_2 - F_1 = F_M'(\rho_M + \rho_H)\rho_M'(r_{M-M}) - F_M'(\rho_M)\rho_M'(r_{M-M}). \qquad (11)$$

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

$$F_2 - F_1 = F_M''(\rho_M)\rho_H\rho_M(r_{M-M}), \qquad (12)$$

where $F_M'' > 0$, $\rho_H > 0$, and $\rho_M' < 0$. 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:

$$\rho(z) = (1/\sqrt{2\pi}\sigma)\sum_i \exp[-(z-z_i)^2/2\sigma^2]$$

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

b) Structure factor $S_l(T)$

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

$$\langle |S_l|^2 \rangle = \langle |1/n_l \sum_i \exp[-ig.r_i]|^2 \rangle,$$

where $\langle\rangle$ denotes the time averaging, n_l is the number of atoms in layer 1, and the sum is over the atoms of layer 1. $\langle |S_l|^2 \rangle$ is calculated for $g = 2\pi/a(1,0)$. Our result for $\langle |S_l|^2 \rangle$ 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. $\langle |S_l|^2 \rangle$ 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.

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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 develope the EAM functions for that system.

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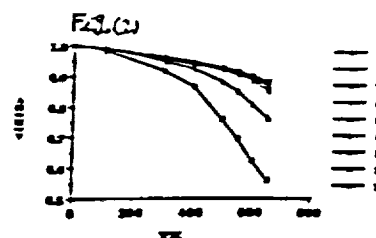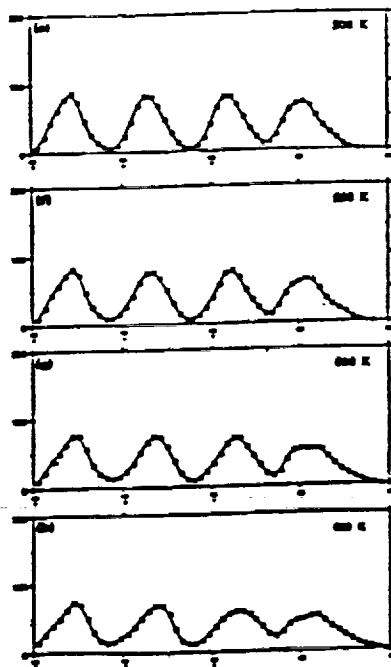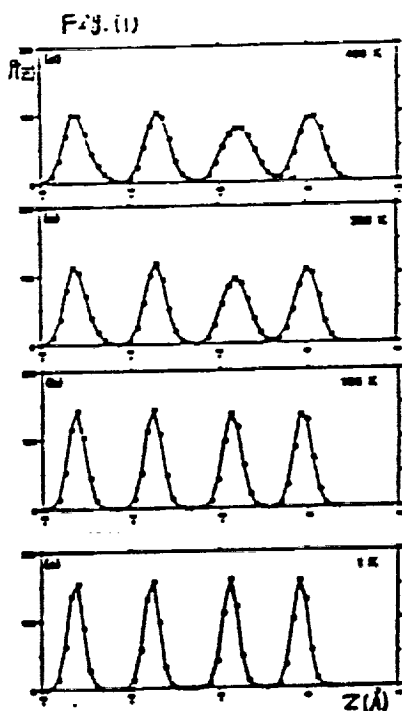6. E. T. Chen, R. N. Barnett, and U. Landman, **Phys. Rev. B41**, 439(1990).

Fig. (1)

Fig. (2)

Table (1)