The Embedded Atom Model and large-scale MD simulation of tin under shock loading

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Abstract. The goal of the work was to develop an interatomic potential, that can be used in large-scale classical MD simulations to predict tin properties near the melting curve, the melting curve itself, and the kinetics of melting and solidification when shock and ramp loading. According to phase diagram, shocked tin melts from bcc phase, and since the main objective was to investigate melting, the EAM was parameterized for bcc phase. The EAM was optimized using isothermal compression data (experimental at T=300 K and ab-initio at T=0 K for bcc, fcc, bct structures), experimental and QMD data on the Hugoniot and on the melting at elevated pressures. The Hugoniot was centred at β-tin at ambient conditions showed that the calculated Hugoniot is in good agreement with experimental and QMD data above β-bct transition pressure. Calculations of overcooled liquid in pressure range corresponding to bcc phase showed crystallization into bcc phase. Since the principal Hugoniot of tin originates from the β-tin that is not described by this EAM the special initial state of bcc samples was constructed to perform large-scale MD simulations of shock loading.

1. Introduction
The objective of the work was to develop an interatomic potential for tin, that can be used in large-scale (billions of particles) molecular dynamics simulations to predict tin properties near the melting curve, the melting curve itself, and kinetics of melting and solidification under different conditions of loading. The construction of such a potential is complicated by the fact that tin enters group IV of the periodic table, standing between elements which have a diamond-like structure with strong covalent bonds (C, Si, Ge), and Pb which is stable in its metal phase. This makes its phase diagram rather sophisticated. So, at T=0°C at least three polymorphous transitions with strongly different kinetics are known for tin. A fourth is predicted theoretically but not confirmed in experiment. The EAM was parameterized to fit basic properties of high-pressure bct and bcc phases of tin. Actually, we don’t make difference between bct and bcc and consider them as single phase due to the closeness of their properties. When fitting parameters of the EAM we took into account phase stability relative to other crystal structures (hcp and fcc), melting curve at pressure range 10-100 GPa, isothermal compression and the Hugoniot. To carry out MD simulations of shock wave loading one needs to build a sample of material which initial state corresponds to β-tin at ambient conditions. But our EAM potential does not describe β-tin. Tin in bcc phase at ambient conditions has parameters which are quite different from the experimental Hugoniot centred at $\rho_{β}=7.29$ g/cm³, $E_{β}^0=-3.12$ eV/atom. Here we choose special initial state of bcc tin in such a way as to reproduce experimental Hugoniot in the regions of stability of bcc and bct phases (the last one is the slightly distorted bcc).
2. Mathematical form of the EAM potential

Hereafter we present the functional form of the EAM that was chosen in the current work. Potential energy is written as:

\[ U_i(\vec{r}_i, \vec{r}_{i_2}, ..., \vec{r}_N) = AE^{(coh)}F(\rho_i(\vec{r}_i, \vec{r}_{i_2}, ..., \vec{r}_N)) + \frac{1}{2} \sum_{j<i} \phi(r_{ij}), \]

where \( A \) – empirical parameter, \( E^{(coh)} \) – cohesive energy, \( \rho_i(\vec{r}_i, \vec{r}_{i_2}, ..., \vec{r}_N) \) – normalized total electron density at the position of \( i \)-th atom. Embedding function has Johnson's form [1]:

\[ F(\rho_i) = -\left(1 - \ln \rho_i^*\right)\rho_i^*, \]

where \( n \) – empirical parameter. Total electron density at the position of \( i \)-th atom is normalized by factor \( Z \) – number of neighbours in so called “reference structure”:

\[ \rho_i = \frac{\bar{\rho}_i^0}{Z}. \]

Total electron density is the sum of partial electron densities:

\[ \bar{\rho}_i^0 = \sum_{j(i)} \psi^{(0)}(r_{ij}). \]

Radial function of partial density is smoothly reduced to zero at the given distance ( \( r_{max} \)):

\[ \psi^{(0)}(r) = S \left( \frac{r_{max} - r}{r_{max} - r_{min}} \right) \psi^{(0)}(r), \]

where \( S(x) = \begin{cases} 0, & x \leq 0 \\ 35x^4 - 84x^5 + 70x^6 - 20x^7, & 0 < x < 1 \\ 1, & x \geq 1 \end{cases} \)

Partial electron density is written in the exponential form:

\[ \psi^{(0)}(r) = \exp \left( -\beta^{(0)} \frac{r - r_0}{r_0} \right), \]

where \( \beta^{(0)} \) – attenuation rate, \( r_0 \) – characteristic radius. The pair-wise function is introduced in such a way as to reproduce the equation of state of the simplest phase and is written as:

\[ \phi(r) = E_0 + 2 \frac{E^{(coh)}}{Z} E^*(r), \]

where \( E^* \) – the modified Rose function:

\[ E^*(r) = - \left(1 + \alpha x + \eta x^2 + \mu x^3 + D(\alpha x)^3 \frac{r_0}{r} \right) \exp(-\alpha x), \]

where \( x(r) = \frac{r - r_0}{r_0} \) is the microscopic strain.

3. EAM parameters optimization

The model described above was implemented in MOLOCH MD code [2]. The following information was used to fit EAM parameters:

- experimental P-\( \rho \) Hugoniot of tin centred at \( P=0 \), \( \rho_0=7.29 \) g/cm\(^3\), \( E_0=-3.12 \) eV [3] (these parameters correspond to \( \beta \)-tin at ambient conditions);
- isothermal compression curve \( T=300 \) K;
- experimental and \textit{ab-initio} MD data on melting curve at elevated pressures;
- \textit{ab-initio} MD data on temperature along the Hugoniot [4].
The EAM parameters obtained after the optimization procedure are presented in table 1.

It was also interesting to check whether the parameterization of the EAM provides for the crystallization into bcc phase from the melt. We carried out a series of calculations of crystallization in the pressure range from 10 to 100 GPa. Crystal structure was analyzed by ATA (Adaptive Template Analysis) [5]. Recrystallization into bcc lattice during cooling down the melt was confirmed.

Table 1. Two sets of parameters for tin potential.

| Parameter | $E^{(coh)}$ | $A$ | $n$ | $Z$ | $r_{\text{max}}$ | $r_{\text{min}}$ | $\beta^{(0)}$ | $r_0$ |
|-----------|-------------|-----|-----|-----|-----------------|-----------------|-------------|-------|
| Set 1     | 1.8475 eV   | 1.401| 0.724| 7.618| 5.599 Å         | 1.0 Å           | 6           | 3.437 Å |
| Set 2     | 1.8475 eV   | 1.401| 0.724| 7.618| 5.599 Å         | 1.0 Å           | 6           | 3.437 Å |

| Parameter | $E_\theta$ | $\alpha$ | $D$ | $\eta$ | $\mu$ |
|-----------|------------|-----------|-----|--------|-------|
| Set 1     | 0.30625 eV | 3.314     | 0   | 2.41   | 0     |
| Set 2     | 0.32190 eV | 3.072     | 0.145| 2.72   | -1.87 |

4. Comparison of EAM with experimental and \textit{ab-initio} data

Figure 1 presents results of melting line calculation with the thermodynamic integration technique. Here we also plotted the Hugoniot calculated with the Set 2 of EAM parameters presented in table 1 to compare it with the Hugoniot calculated with the Set 1. The current melting curve takes a middle position between the extrapolation of DAC data [6] and data from dynamic experiments [7] and \textit{ab-initio} MD calculations [4]. In figure 2 we also plotted the Hugoniots and isotherms in (V-P) plane calculated with Set 1 and Set 2 parameterizations of the EAM. One can see that the Set 2 parameterization actually did not change the isotherm but improved the Hugoniot.

Figure 1. Hugoniot in (P-T) plane. Calculations with the EAM (this work): light blue solid circles – estimates of melting at different pressures for Set 2 (Heat and wait method); blue squares – MD Hugoniot for Set 1; blue triangles – the Hugoniot for Set 2; red line – equilibrium melting line (thermodynamic integration technique) for Set 2. Black diamonds – quantum MD data on melting line [4]. Experimental data: black triangles – DAC data on melting line [6]; black dashed line – extrapolation of DAC data on melting line according to Simon melting equation; black open circles and thin black dotted line – melting curve [7], open black squares – melting points [8], black star – melting onset on the Hugoniot [9]. Solid black line – temperature along the Hugoniot [9]. Green dotted line is tentative equilibrium lime between bct and bcc tin [9].
To carry out large-scale MD simulations of shock wave loading one needs to build a sample of material initial state of which corresponds to $\beta$-tin at ambient conditions. But current version of the EAM potential does not describe $\beta$-tin. Tin in bcc phase at ambient conditions has the following parameters: $\rho_{\text{bcc}}^0=7.775 \text{ g/cm}^3$, $E_{\text{bcc}}^0=-3.0214 \text{ eV/atom}$, which are quite different from the principal Hugoniot centred at $\rho_{\beta}^0=7.29 \text{ g/cm}^3$, $E_{\beta}^0=-3.12 \text{ eV/atom}$ (see [3]). We propose here to choose special initial state of bcc tin in such a way as to reproduce experimental Hugoniot in the regions of stability of bcc and bct phases (the last one is slightly distorted bcc). Our attempts have resulted in:

- changing initial temperature from 300 K to 100 K;
- ascribing initial porosity ~5% (see figure 4).

The Hugoniot calculated for this particular initial state is plotted in figure 3. The calculations were performed with the Hugoniotstat technique. When solving Hugoniot equation we assumed $E_{\text{bcc}}^0=-3.0214 \text{ eV/atom}$ and $\rho_{\beta}^0=0.95 \rho_{\text{bcc}}^0=7.3863 \text{ g/cm}^3$. We assumed also that pores collapse at rather small pressures and that the kinetics of the collapse may be neglected. Obtained Hugoniot slightly differs from the Hugoniot centred at $\beta$-tin parameters at ambient conditions, but in (P, T) plane it almost coincides with the data from [9]. In $(p, P)$ and $(D, U)$ planes it is also in satisfactory agreement with experimental data (see figure 6 and figure 8). That is why we fixed initial temperature and porosity as

Figure 2. Hugoniotics and isotherms in (V-P) plane.

Solid red and blue red lines – the Hugoniot and isotherm of bcc tin respectively calculated with Set 2 parameterization of the EAM, red and blue dashed lines – the Hugoniot and the isotherm calculated with Set 1. Exp. data: red dots – the Hugoniot [10], black squares – isothermal compression [11], black circles – isothermal compression [12], black diamonds – isothermal compression [13].

Figure 3. Hugoniotics in (P-T) plane. Blue line Hugoniotstat calculations with the EAM (this work) for $T=100$ K and 5% porosity. Red solid line – temperature along the Hugoniot according to [9].

Figure 4. Tin monocrystalline sample with 5% porosity. Atoms in randomly placed spheres with $R=10\text{Å}$ were deleted.
100 K and 5% respectively, hence, in principle, it would be possible to provide for more exact agreement with the principle Hugoniot of bcc tin obtained with current EAM parameterization.

The next step was to check whether the Hugoniot obtained with the Hugoniostat is reproduced in direct MD simulations of shock loading. In other words whether our assumption of neglecting pore collapse kinetics is correct. We performed a number of shock wave simulations with the samples 500x100x100 unit cells and piston velocities in the range 200–2000 m/s. Parameters of the shock waves in these simulations were taken after waves gained stationary character (linear dependence of the shock front position upon time, see figure 5). Results of direct MD calculations are plotted in figures 6-8 together with the results of the Hugoniostat calculations.

![Figure 5. Shock front position as a function of time for different piston velocities.](image)

![Figure 6. Tin Hugoniots. Black dots – experiment, blue curve – Hugoniostat for T=100 K and 5% porosity, red curve – shock loading for T=100 K and 5% porosity.](image)

![Figure 7. Tin Hugoniots. Black dots – isentropes, orange curve – quasi isentrope (Hugoniostat), blue curve – Hugoniostat for T=100 K and 5% porosity, red curve – shock loading for T=100 K and 5% porosity.](image)

![Figure 8. Shock wave velocity as a function of piston velocity. Black dots – experiment, blue curve – Hugoniostat for T=100 K and 5% porosity, red curve – shock loading for T=100 K and 5% porosity.](image)

In the regions of phase diagram corresponding to pure solid (below 40 GPa) and liquid (above 65 GPa) states the Hugoniostat and direct shock wave simulation data are in very good agreement. The difference is in the onset of melting – in direct simulations it takes place earlier. The matter is that in direct simulations when the shock wave propagates through the sample pores collapse and as a result...
local increase in temperature takes place. As a consequence material melts in the vicinity of collapsed pores even if the bulk state of a sample is still below the equilibrium melting line. In several picoseconds temperature in the vicinity of collapsed pores equilibrates with the rest of the sample and resulted equilibrium temperature is less than melting temperature at the given pressure. But the process of recrystallization from the melt is rather slow and the regions of overcooled liquid remain in the bulk of the sample. In other words the sample is nonequilibrium mixture of the solid and the liquid. As the intensity of loading increases the bulk of the material melts behind the shock front and the Hugoniotstat and direct shock wave simulation data coincide.

5. Conclusion

Quick interatomic potential for tin with two sets of parameters was built on the basis of Embedded Atom Model. All necessary information for implementation of the potential into a MD code is provided. The potential quite well reproduces properties of high-pressure bct and bcc phases of tin (the Hugoniot and isothermal compression). As for the data on the melting curve at elevated pressures there is a good deal of discrepancy between static and dynamic experimental data. Actually there are two groups of data corresponding to low- and high temperature melting at a given pressure. Ab-initio molecular dynamics also gives high-temperature melting [4]. Calculated with current EAM melting curve takes intermediate position but tends to high-temperature data and at the pressure of melting on the Hugoniot it correspond to experimental data [8].

6. References

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