Application of embedded atom model to the liquid metals

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Abstract. The productive method of creation the inter-particle potential in Embedded Atom Model (EAM) is presented that uses directly the structure data of liquid metal near the melting point. The embedding potential is written as the power series of the difference between the effective EAM electronic density $\rho$ and its standard value $\rho_0$ ($\rho_0$ is taken as 1). The mean value $<\rho> = \rho_0$ in the standard state of a liquid (usually near the melting point). At this definition of EAM potential, the pair term in potential coincides with the effective pair potential that can be reconstructed using the pair correlation function (PCF) of liquid metal (for example with Schommers algorithm). The parameters of embedding part of potential are determined using the potential energy of liquid in the standard state, module of compression and parameters of a liquid in any extreme state (at high temperature or pressure). The method presented was applied to the creation of EAM potentials and simulations of liquid metals bismuth, gallium, mercury, rubidium, cesium, iron and iron – sulfur solutions in wide intervals of parameters, including states near the critical point (bismuth, gallium, mercury, rubidium and cesium) and at the conditions of Earth core. The accuracy of predictions of structure properties, thermodynamic properties and diffusivity is rather good. EAM potentials constructed especially for liquid metals describe their properties in wide temperature and pressure limits much better than the EAM potentials created for crystal metals. In the states typical for the shock waves tests (at very strong compression) crystal metal EAM potentials may give very erroneous pressure data.

1. Introduction

In recent years, the embedded atom model (EAM) has been used fairly extensively in crystalline metal simulation. This model includes collective interactions. The potential energy of a metal is written in the form (e.g., see [1]):

$$U = \sum_i \Phi(\rho_i) + \sum_{i<j} \varphi(r_{ij})$$

(1)

where $\Phi(\rho_i)$ is the “embedding potential” of the $i$-th atom, which depends on the effective electron density $\rho$ at the center of the atom, and the second sum over pairs of atoms is the usual pair potential. The effective electron density is created by the surrounding atoms. It is written as

$$\rho_i = \sum_j \psi(r_{ij})$$

(2)

where $\psi(r_{ij})$ is the contribution of neighbour $j$ to the electron density. Calculations use three adjustment functions, $\Phi(\rho_i)$, $\psi(r)$ and $\varphi(r)$. There is therefore considerable opportunity for fitting the calculated properties to experiment. With crystals, where the nearest inter-atomic distances at equilibrium are few, the model allows density, energy, elastic constants, vacancy formation energy, surface properties, etc. to be described correctly.

The embedded atom model was also applied to liquid metals and alloys. Embedded atom potentials were used in [2–4] to determine the static structure factors and some thermodynamic properties of liquid transition metals. In [5], similar calculations were performed for liquid Cu, Ag, Au, Ni, Pd, and Pt; agreement with the diffraction structure factors and the energies and entropies of the liquids close to the melting points of the metals was obtained. A method for liquid iron simulation with the use of dif-
fraction structural data was developed in [6]. Another EAM potentials were used to simulate liquid Ga and Bi [7], mercury [8], and iron at high temperatures and pressures [9].

With liquid or amorphous metals, an important role is played by the main structural characteristic, the pair correlation function (PCF). The structural characteristics of real metals and their models are usually compared by comparing their PCF’s. The degree to which two PCF’s \( g_1(r) \) and \( g_2(r) \) are different is determined as the standard deviation (residual) calculated by the equation

\[
R_g = \left\{ \frac{1}{n_2-n_1+1} \sum_{n_1}^{n_2} \left[ g_1(r_i) - g_2(r_i) \right]^2 \right\}^{1/2}
\]

where \( n_1 \) and \( n_2 \) are the lower and upper values for the compared histogram points. If the residual is on the order of 0.01, two PCF plots are almost indistinguishable visually. Embedded atom model potentials obtained for crystalline metals are sometimes inapplicable to their melts [7]. It is therefore expedient to develop a special technique for selecting embedded atom potentials of liquid metals. Such potentials should correctly describe both the thermodynamic properties and structure of liquids. This technique should include the possibility of using diffraction structural data. Two different variants of the corresponding procedure were suggested in [6-9].

2. Method of calculations

The selection of the \( \Phi(\rho) \), \( \psi(r) \) and \( \varphi(r) \) functions is not unambiguous. We can therefore use various function forms. The usual form of this function is as follows: it starts from zero into the negative region as \( \rho \) grows, passes a minimum, and then begins to increase. In metal simulations by the method of molecular dynamics the effective \( i-j \) pair force in a one-component system is given by

\[
F_{ij} = -\left[ \frac{\partial \Phi}{\partial \rho_i} \right] \rho_i + \left( \frac{\partial \Phi}{\partial \rho_j} \right) \rho_j - \frac{\partial \psi(r)}{\partial r} r_{ij} - \frac{\partial \varphi(r)}{\partial r} r_{ij}
\]

The first sum is the result of embedding potential action, and the second is the contribution of the pair potential. The \( \partial \psi/\partial r \) derivative is negative by the meaning of the \( \psi(r) \) function. The \( d \Phi / d\rho \) derivative is negative in low-density and positive in compressed states. By analogy with [7-9], we selected fairly simple \( \Phi(\rho) \) and \( \psi(r) \) functions for liquid metals,

\[
\psi(r) = \rho_1 \exp(-\rho r)
\]

\[
\Phi(\rho) = a_1 + a_2 (\rho - \rho_0)^2 + a_3 (\rho - \rho_0)^3 \quad \text{at} \quad \rho \geq \rho_1
\]

\[
\Phi(\rho) = b_0 + b_1 (\rho - \rho_1) + b_2 (\rho - \rho_1)^2 + b_3 (\rho - \rho_1)^3 \quad \text{at} \quad \rho < \rho_1
\]

The \( \Phi(\rho) \) function itself and its first derivative are continuous at \( \rho = \rho_1 = 0.9\rho_0 \). This allows the \( b_0 \) and \( b_1 \) coefficients to be written as functions of \( a_1, a_2, a_3 \). As a result, the embedded atom model potential is determined by parameters \( \rho_1, \rho_2, a_1, a_2, a_3, b_2, b_3 \), which makes it possible in principle to fit such properties of the model as density, potential energy (atomization energy), bulk compression modulus, and thermal expansion coefficient to experimental data. Equations (6) and (7) are the initial portions of the expansions of \( \Phi(\rho) \) and may be corrected for a given metal. Below, we assume that \( \rho_0 = 1 \).

Equations (6) and (7) are used to simulate states with elevated and lowered densities, respectively. The \( a_1 \) parameter is largely determined by the potential energy value, \( a_2 \), by the bulk modulus, and \( a_3 \) can be adjusted using the thermal expansion coefficient or density in some high-temperature or compressed state.

There, however, remains such an important property of liquids as their structure, which is primarily characterized by the form of the PCF. To reproduce the structure of a liquid, we must correctly select the pair inter-particle potential \( \varphi(r) \). The scheme of calculations suggested in [7-9] was as follows. Let the standard state be selected close to the temperature of fusion, and let \( \langle \rho \rangle \) denote the mean electron density \( \rho \) at the atoms and \( \Phi(\langle \rho \rangle) \) be the mean \( \Phi(\rho) \) value for the given state of the liquid. At the stage of selecting potentials, the sum of the derivatives \( s = \partial \Phi(\rho)/\partial \rho + \partial \Phi(\rho)/\partial \rho \) can approximately...
be replaced in (4) by the mean value of this sum over all particles $2\phi_\rho / \rho = \langle \rho \rangle$. On this assumption, Eq. (4) for the total effective force can be written as

$$F(r) = - \frac{d\phi_{\text{total}}}{dr} = -2 \frac{d\phi_{\rho}}{dr} \frac{d\psi}{dr} \frac{d\rho}{dr}$$  \hspace{1cm} (8)$$

where $\phi_{\text{total}}$ is the total effective potential, which determines the structure of the liquid, and the $d\phi_{\rho} / dr$ derivative is calculated at $\rho = \langle \rho \rangle$. The $\phi_{\text{total}}$ function can be calculated in different ways from the known PCF (we use the Schommers algorithm [10,11]). The $p_1$ parameter was determined to satisfy the equality $\langle \rho \rangle = \rho_0 = 1$ for the model of the liquid at the temperature of fusion. According to (6), we then have $d\phi_{\rho} / dr = 0$ at $\rho = 1$, and it then follows from (8) that $d\phi_{\text{total}} / dr = d\phi_{\text{total}} / dr$. Since both these potentials tend to zero at large distances, it is clear that $\phi(r) = \phi_{\text{total}}(r)$.

In our calculations, $p_2$ in (5) was an adjustment parameter. It was assumed that $p_2$ was inversely proportional to the coordinate of the first pair correlation function peak, and the results obtained in [7-9] were used. With $p_2$ selected this way, the $\psi(r)$ functions of various metals damp approximately equally in moving from the first to second coordination sphere. The other parameters can be found, for instance, from the known values of density, energy of vaporization, bulk modulus, and thermal expansion coefficient.

3. Liquid Rubidium

The following values of potential parameters were calculated in [12] for liquid Rb: $p_1 = 4.4400$, $p_2 = 0.8192$, $a_1 = -0.4061$, $a_2 = 0.1111$, $a_3 = -0.0080$, $b_0 = -0.404981$, $b_1 = -0.022460$, $b_2 = -0.091400$, $b_3 = -0.860667$. At small $\rho$ values ($\rho < 0.25$), approximation (7) had to be corrected, because (7) gives $\Phi(0) = 0.16174$ instead of zero at $\rho = 0$. The embedded atom model potential with the parameters specified above was used to construct a molecular dynamics model of liquid rubidium at 313 K with a normal density of 1.476 g/cm$^3$. The model contained 1968 atoms in the basic cube with a 57.412 Å edge length. The cutoff radius of pair contributions to the inter-particle interaction and embedding potentials was 14.35 Å. Properties were averaged over a series of runs 1000 time steps long. At the parameters specified, the pressure of the system was very low on the atomic scale (0.0165 ± 0.0032 GPa, the actual pressure being 0.0001 GPa). The discrepancy between the model and diffraction pair correlation functions was $R_g = 0.0162$, which was close to the discrepancy for the model constructed using the Schommers algorithm. The PCF of liquid rubidium model at 313 K is shown in Fig.1. The residual $R_g$ being very small (0.0162), this function almost coincides with the diffraction function. The potential energy $U_{\text{pot}}$ values (with respect to ideal gas) can be compared with the enthalpies of real rubidium after subtracting the kinetic contributions $(3/2)RT$ from them. Agreement between the potential energies calculated for the embedded atom models and the experimental values is quite satisfactory along the liquid–vapor equilibrium line up to 1000 K (the discrepancies do not exceed 2.4%) but worsens as the temperature increases to 1600–2000 K.

The reason for this is a slower increase in the heat capacity $C_v$ of embedded atom models compared with the experimental heat capacity. The mean $C_v$(EAM) and $C_v$(expt) values are 27.0 and 33.3 J/(mol K), respectively, at 1000–1400 K and 37.9 and 44.1, respectively, at 1600–1800 K. The deviations from the experimental data at lowered densities are caused by the metal–nonmetal transition and can be removed by introducing the corresponding corrections into the potential. The calculated bulk compression modulus $K_T$ is in satisfactory agreement with the experimental values at temperatures up to 1000 K. At higher temperatures, the error in $K_T$ obtained in molecular dynamics experiments becomes fairly large because of a very weak volume dependence of pressure and strong pressure fluctuations. $K_T$ values becomes smaller than 0.1 GPa at 1600 K.
The potential obtained above was used to construct liquid rubidium models under various conditions. Simulations were performed by the method of molecular dynamics with maintaining the required temperature and density or pressure. At high pressures, the atoms of a liquid more closely approach each other. For instance, at 570 K and 6.1 GPa, the shortest inter-particle distance found from the PCF was 3.15 Å [13], whereas at 313 K and normal pressure, this distance was 3.75 Å. For this reason, the pair potential calculated using the Schommers method at 313 K had to be continued to smaller distances. This required the introduction of corrections into the pair potential to the left of the 3.75 Å distance. After including these corrections, the diffraction [13] and model PCF’s of rubidium at pressures of 3.9 and 6.1 GPa are in reasonable agreement (the residuals 0.113 and 0.178). The discrepancies may be higher under these conditions than at 313 K because of errors in the embedding potential form and large experimental errors in structure factor. The pressure data are also in agreement: at the density 2.84 g/cm$^3$ and T = 570 K the model pressure is 6.113 GPa against the experimental pressure of 6.1 GPa [13].

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