Computer simulation of liquid cesium using embedded atom model

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Abstract. The new method is presented for the inventing an embedded atom potential (EAM potential) for liquid metals. This method uses directly the pair correlation function (PCF) of the liquid metal near the melting temperature. Because of the specific analytic form of this EAM potential, the pair term of potential can be calculated using the pair correlation function and, for example, Schommers algorithm. Other parameters of EAM potential may be found using the potential energy, module of compression and pressure at some conditions, mainly near the melting temperature, at very high temperature or in strongly compressed state. We used the simple exponential formula for effective EAM electronic density and a polynomial series for embedding energy. Molecular dynamics method was applied with L. Verlet algorithm. A series of models with 1968 atoms in the basic cube was constructed in temperature interval 323-1923 K. The thermodynamic properties of liquid cesium, structure data and self-diffusion coefficients are calculated. In general, agreement between the model data and known experimental ones is reasonable. The evaluation is given for the critical temperature of cesium models with EAM potential.

1. Introduction
We used the following expressions for EAM potential. 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 \( \Phi(\rho) \) is the “embedding potential” of the \( i \)-th atom, which depends on the effective electron density \( \rho \) (dimensionless) 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

\[ \rho_i = \sum_j \psi(r_{ij}) , \]

where \( \psi(r_{ij}) \) is the contribution of neighbour \( j \) to the effective electron density. Calculations use three adjustment functions, \( \Phi(\rho) \), \( \psi(r) \) and \( \varphi(r) \). Previously rather few works on the liquid metals simulation were published. EAM potentials obtained for crystalline metals are sometimes inapplicable to their melts [2]. It is therefore expedient to develop a special technique for creation EAM potentials of liquid metals. Such potentials should correctly describe both the thermodynamic properties and structure of liquids. We apply here the method of EAM potential constructing that uses directly the main structure characteristics of a liquid – pair correlation function (PCF). This method was successful in the simulation of liquid metals Ga, Bi [2], Hg [3], Fe [4], Rb ([5] and this Conference) and Pb [6] in very wide range of temperatures and pressures.

The structural characteristics of real liquid metals and their models are usually compared by comparing their PCF’s. The degree to which two PCF’s \( g_1(r) \) and \( g_2(r) \) (model and diffraction ones) are different is determined as the standard deviation (residual) calculated by the equation
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. Therefore the value of \( R_g \) is a measure of adequacy of liquid metal model. Our method of the constructing EAM potential includes the possibility of using diffraction structural data directly.

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 with the method of molecular dynamics the effective pair force in a one-component system is given by

\[
F(r) = -\partial \psi(r) - \gamma \rho \delta \rho
\]

The first sum is the result of embedding potential action, and the second is the contribution of the pair potential. The \( \partial \psi(r) \) derivative is negative by the meaning of the \( \psi(r) \) function. The \( \partial \Phi(\rho) \) derivative is negative in low-density and positive in compressed states. By analogy with [2-4], we selected fairly simple \( \Phi(\rho) \) and \( \psi(r) \) functions for liquid cesium,

\[
\psi(r) = p_1 \exp(- p_2 r)
\]

\[
\Phi(\rho) = a_1 + a_2 (\rho - \rho_0)^2 + a_3 (\rho - \rho_0)^3
\]

\[
\Phi(\rho) = \alpha \rho^m + \beta \rho^p
\]

Here \( \rho_1 < \rho_0 \) and \( \rho_2 > \rho_0 \). The \( \Phi(\rho) \) function itself and its first derivative are continuous at \( \rho = \rho_1 \) and \( \rho = \rho_2 \). This allows \( \alpha, \beta, \gamma \) and \( \delta \) coefficients to be written as functions of \( a_1, a_2, a_3 \) if \( \rho_0, \rho_1, \rho_2, m \) and \( n \) are known. As a result, the EAM potential is determined by parameters \( p_1, p_2, a_1, a_2, a_3, \rho_0, \rho_1, \rho_2, m, n \) 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. Below, we assume that \( \rho_0 = 1 \).

Equations (6) and (8) are used to simulate states with lowered and elevated densities, respectively. The \( a_1 \) parameter is 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 [2-4] was as follows. Let the standard state be selected close to the temperature of fusion, and let \( <\rho> \) denote the mean electron density \( \rho \) at the atoms and \( \Phi(<\rho>) \) be the mean \( \Phi(\rho_i) \) 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 \( 2\partial \Phi(\rho)/\partial \rho \) at \( \rho = <\rho> \). On this assumption, Eq. (4) for the total effective force can be written as

\[
F(r) = -\frac{d\Phi(\rho)}{d\rho} = -2 \frac{d\Phi(\rho)}{d\rho} \frac{d\varphi}{dr} - \frac{d\varphi}{dr}
\]
where \( \varphi_{\text{total}} \) is the total effective potential, which determines the structure of the liquid, and the \( d\Phi(\rho)/d\rho \) derivative is calculated at \( \rho = <\rho> \). The \( \varphi_{\text{total}} \) function can be calculated in different ways from the known PCF (we use the Schommers algorithm [7, 8]). The \( p_1 \) parameter was determined to satisfy the equality \( <r> = r_0 = 1 \) for the model of the liquid at the temperature of fusion. According to (7), we then have \( d\Phi(\rho)/d\rho = 0 \) at \( \rho = 1 \), and it then follows from (9) that \( d\varphi/dr = d\varphi_{\text{total}}/dr \). Since both these potentials tend to zero at large distances, it is clear that \( \varphi(r) = \varphi_{\text{total}}(r) \).

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 [2-4] were used. The other parameters can be found, for instance, from the known values of density, energy of vaporization, bulk modulus, and other data.

### 3. Liquid Cesium

The pair potential of liquid cesium was calculated using Schommers algorithm (See Fig.1). The following values of potential parameters were calculated for liquid Cs: \( p_1 = 4.4960 \), \( p_2 = 0.7358 \), \( a_1 = -0.3668 \), \( a_2 = 0.1220 \), \( a_3 = -0.0664 \), \( \alpha = -0.6712 \), \( \beta = -0.6712 \), \( \gamma = -2.1820 \), \( \delta = 1.8236 \), \( \rho_0 = 1 \), \( \rho_1 = 0.8 \), \( \rho_2 = 1.45 \), \( m = 2.80 \), \( n = 0.85 \). The values \( a_1 \), \( a_2 \), \( a_3 \), \( \alpha \), \( \beta \), \( \gamma \), \( \delta \) are in eV. The EAM potential with the parameters specified above was used to construct a molecular dynamics model of liquid cesium at 323, 573, 773, 1073, 1173, 1373, 1673 and 1923 K with experimental densities. All models contained 1968 atoms in the basic cube. The cutoff radius of pair contributions to the inter-particle interaction and embedding potentials was 13.15 Å. The data obtained using the molecular dynamics are shown in the Table 1.

| \#  | T, K | \( d \), g/cm\(^3\) | \( p \), MPa | \( R_g \) | \(-U_{\text{pot}}, \text{kJ/mol}\) | \( K_r \), GPa | \( D10^7 \), cm/s |
|-----|-----|-----------------|--------|--------|-----------------|-----------|-------------|
|     |     |                 |        |        | EAM             | EAM       | EAM        |
|     |     |                 |        |        | Exper [9]       | Exper [9] | Via S-E    |
| 1   | 323 | 1.83            | 84     | 0.033  | 68.87           | 70.0      | 1.87       |
|     |     |                 |        |        |                 | 1.19      | 2.39       |
| 2   | 573 | 1.68            | 11     | 0.033  | 64.43           | 65.2      | 1.22       |
|     |     |                 |        |        |                 | 1.23      | 8.48       |
| 3   | 773 | 1.57            | 3.4    | 0.021  | 61.02           | 61.8      | 0.89       |
|     |     |                 |        |        |                 | 0.88      | 16.7       |
| 4   | 1073| 1.39            | 2.7    | 0.022  | 55.86           | 56.7      | 0.60       |
|     |     |                 |        |        |                 | 0.58      | 29.1       |
| 5   | 1173| 1.33            | -0.7   | 0.015  | 54.25           | 54.8      | 0.54       |
|     |     |                 |        |        |                 | 0.50      | 36.4       |
| 6   | 1373| 1.21            | -3.2   | 0.025  | 50.39           | 50.4      | 0.28       |
|     |     |                 |        |        |                 | 0.35      | 49.8       |
| 7   | 1673| 0.956           | -3.9   | 0.054  | 44.60           | 41.8      | 0.15       |
|     |     |                 |        |        |                 | 0.14      | 76.5       |
| 8   | 1923| 0.590           | 6.2    | 0.160  | 35.18           | 31.6      | < 0.01     |
|     |     |                 |        |        |                 | -         | 119        |

At the parameters specified, the pressure of the models is very low on the atomic scale. The residuals between the model and diffraction PCF’s are rather small at all temperatures except 1923 K. The PCF’s of liquid cesium models at 323-1373 K are very close to diffraction ones. Agreement between the potential energies calculated for the EAM models and the experimental values is quite satisfactory.

Fig.1. Pair potential of liquid cesium
along the liquid–vapor equilibrium line up to 1373 K but worsens something as the temperature increases to 1673–1923 K. The calculated bulk compression modulus $K_T$ is in good agreement with the experimental values at temperatures up to 1673 K. $K_T$ value becomes smaller than 0.01 GPa at 1923 K. The self-diffusion coefficients $D$ agree very well with the values calculated via Stokes-Einstein equation (S-E in the Table) using the experimental viscosity data. The temperature dependence $D(T)$ is described by the power formula $D = 1.4896 \times 10^{-10} T^{2.0820}$. Critical temperature was evaluated using the temperature dependence of the dispersion of Voronoi polyhedrons volume distribution; it is near 2000 K in accordance with experimental data.

The potential obtained above was used to construct liquid cesium models under high pressures. Simulations were performed by the method of molecular dynamics with maintaining the required temperature and density. At high pressures, the coordinates of PCF 1st peak agree well with experimental data [10] (See Table 2) but drastic drop of coordination number to 7-8 at the pressures greater than 4 GPa isn’t observed in the models. Good agreement is obtained between experimental and calculated values of the pressure up to 9-10 GPa. The self-diffusion coefficient diminishes at the compression of cesium in 2 – 3.5 times. The values of self-diffusion coefficient show that the models are liquid at these conditions.

| $T$, K | V/N, cm$^3$/mol | P, GPa | $U_{\text{inst}}$, kJ/mol | $r_1$, Å | Coordination number | D $10^5$, cm$^2$/s |
|-------|----------------|--------|---------------------------|--------|---------------------|-----------------|
|       | Model | Exp$^*$ |       | This work | [ 10] |                    |                 |
| 493   | 49.8  | 1.32   | 1.6  | -55.9 | 4.45 | 4.6 | 15.9 | 8.24 |
|       | 39.9  | 2.98   | 3.3  | -37.1 | 4.09 | 4.2 | 12.3 | 7.43 |
|       | 29.9  | 7.22   | -    | 8.06  | 3.85 | 3.7 | 14.1 | 4.41 |
|       | 24.7  | 12.5   | -    | 55.0  | 3.63 | -  | 13.6 | 2.57 |
| 623   | 39.9  | 3.03   | 3.2  | -35.9 | 4.18 | 4.25 | 17.1 | 10.7 |
|       | 29.9  | 7.38   | 6.8  | 8.86  | 3.84 | 3.75 | 14.6 | 6.04 |
|       | 27.15 | 9.76   | 8.8  | 30.5  | 3.78 | 3.7 | 14.4 | 4.73 |

$^*$ - at the error of density evaluation ±7% in [10]. $r_1$ – the coordinate of PCF 1st peak.

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