

STRUCTURE PROPERTIES OF LIQUID FCC TRANSITION METALS USING THE EMBEDDED ATOM METHOD POTENTIAL

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The liquid structure calculations for fcc transition metals using the variational modified hypernetted chain liquid state theory with a new embedded atom method (EAM) model have been presented. In this model, an analytic construction of a many – body potential inspired from the Mishin et. al. [Phys. Rev. B 63, 224106, 2001] potential functions is presented. The new model has been applied to calculate the structural properties of fcc transition metals for Cu, Ag, Au and Ni near their melting points. The computed static structure factors and pair distribution function are in good agreement with the experimental data.

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1. Introduction

In many problems the energies and stability of various crystalline structures of metals can be calculated by ab initio methods [1] or some methods based on fitting the parameters, such as the tight binding (TB) approximation [2], especially the embedded-atom method (EAM) [3] which has been proposed by Daw and Baskes. Many of scientists in material science great interest EAM theory and successfully applied to transition metals in order to obtain impurity, surface, alloys, liquid and mechanical properties. There are several versions of EAM which are different with the parameterisation methods and the functions involved. The parameterisation is also performed by fitting the model to bulk solid properties using the different energy equations of state that generally universal equation of Rose et al. [4] is used. Although the EAM primarily developed for the solid phase has also been used in liquid structure calculations with molecular dynamic (MD) simulations or integral equation theories in order to check the accuracy of the forms chosen for the embedding function and pair interaction and of the method used for their parameterisation. Researchers [5-7] show that one of the self consistent integral equation theory, the variational modified hypernetted chain (VMHNC) approximation [8-10] successfully applied to metallic systems in the EAM calculations. It is for this reason that we choose the VMHNC theory for our liquid structure calculations using the EAM derived effective pair potentials with the recently proposed EAM model potential of Mishin et al. [1] which has been applied for the calculations of structural stability and lattice defects in copper. They have also determined the EAM potential parameters for Cu by fitting on the properties in the solid state.

There are number of other papers that have also used EAM potentials for the liquid structure and thermodynamic properties of a number of transition metals [5-7, 11-15]. However, it has been noted in Ref. [1] that the proposed potential functions were different form from the general EAM potential functions. To our knowledge, the Mishins' EAM potentials has not been yet applied for liquid structure calculations using integral equation theories. This is one of the aims of this work. The

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present work, we have employed this EAM potential functions to evaluate the inter-ionic interaction for liquids Cu, Ag, Au and Ni when the fcc structural energy in their liquid state was required to follow the universal equation of state of Rose et al. [4]. Thus the presented parameterization scheme in this work are different from others which fitted the potential parameters to the properties in the solid state. We have also obtained the structure factors and pair distribution functions for each metal in their liquid state near melting. The second aim is to check the validity of this parameterization scheme of the EAM model potentials for liquid metallic systems. We have shown that the calculated VMHNC liquid structure factors and pair distribution functions for Cu, Ag, Au and Ni are in good agreement with the experimental data.

2. Theory

2.1 Effective pair potential from the embedded-atom method

In the embedded – atom method [EAM], the total energy of a monatomic system is

$$E_{\text{tot}} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \phi(r_{ij}) + \sum_i F(\rho_i) \quad (1)$$

where E_{tot} is the total energy, $\phi(r_{ij})$ is the pair potential between atoms i and j separated by r_{ij} and $F(\rho_i)$ is the embedding energy as a function of the electron density ρ_i at atom i due to all other atoms

$$\rho_i = \sum_{i \neq j} f(r_{ij}) \quad (2)$$

where $f(r_{ij})$ is the electron density distribution function of an atom, namely ‘atomic density’ function. It has been noted [1] that the functional forms of $\phi(r)$, $f(r)$ and $F(\rho)$ are differ from the general forms of the EAM potential functions. The parametrized pair interaction function is

$$\begin{aligned} \phi(r) = & \left[E_1 M(r, r_0^{(1)}, \alpha_1) + E_2 M(r, r_0^{(2)}, \alpha_2) + \delta \right] \times \psi\left(\frac{r-r_c}{h}\right) \\ & - \sum_{n=1}^3 H(r_s^{(n)} - r) S_n (r_s^{(n)} - r)^4. \end{aligned} \quad (3)$$

where

$$M(r, r_0, \alpha) = \exp[-2\alpha(r - r_0)] - 2\exp[-\alpha(r - r_0)] \quad (4)$$

is a Morse function and $H(x)$ denotes a unit step function. In equation (3), $\psi(x)$ is a cut off function defined as $\psi(x) = 0$ if $x \geq 0$ and $\psi(x) = x^4 / (1 + x^4)$ if $x < 0$. A parameter r_c is cut-off distance. $E_1, E_2, r_0^{(1)}, r_0^{(2)}, \alpha_1, \alpha_2, \delta, h, r_c$ and $\{r_s^{(n)}, S_n\}_{n=1,2,3}$ are the fitting parameters. The electron density function in Eq.(2) is given as

$$f(r) = \left[A \exp(-\beta_1 (r - r_0^{(3)})^2) + \exp(-\beta_2 (r - r_0^{(4)})^2) \right] \times \psi\left(\frac{r-r_c}{h}\right) \quad (5)$$

where A , $r_0^{(3)}$, $r_0^{(4)}$, β_1 and β_2 are fitting parameters. In present paper, for the purpose of liquid state calculations the value of cut-off distances r_c used in the determination of the effective pair interaction of liquid fcc transition metals are taken from recent liquid state calculations of Bhuiyan et al. [5]. Following Bhuiyan, it is assumed that the effective interactions are significant only the first three nearest neighbour shells and cut-off both $f(r)$ and $\phi(r)$ at the value of r_c . At this point, the cut-off function $\psi(x)$ in Eqs. (3, 5) guarantees that the functions $\phi(r)$, $f(r)$ and their slope are zero at the cut-off distance r_c .

$$\phi(r_c) = 0, \quad f(r_c) = 0 \quad (6-a)$$

$$\phi'(r_c) = 0, \quad f'(r_c) = 0 \quad (6-b)$$

The embedding function $F(\rho)$ is taken as

$$F(\rho) = F^{(0)} + \frac{1}{2}F^{(2)}(\rho-1)^2 + \sum_{n=1}^4 q_n(\rho-1)^{n+2} \quad (7)$$

for $\rho < 1$ and

$$F(\rho) = \frac{F^{(0)} + \frac{1}{2}F^{(2)}(\rho-1)^2 + q_1(\rho-1)^3 + Q_1(\rho-1)^4}{1 + Q_2(\rho-1)^3} \quad (8)$$

for $\rho > 1$. In the above equations the coefficients $F^{(0)}$ and $F^{(2)}$ can be determined from the following equations.

$$F(\rho_c) = E_{\text{EOS}}(a^*) - \frac{1}{2}\sum\phi(r_c). \quad (9)$$

where $E_{\text{EOS}}(a^*)$ is Rose's equation of state (EOS) for the cohesive energy near the melting point for liquid metals [5]. The Born stability condition can be written as

$$r \frac{d}{dr} \left[F(\rho) + \frac{1}{2}\sum\phi \right]_{r=r_c} = 0 \quad (10)$$

where r_c is the cut - off distance. Overall this parameterization scheme 23 free fitting parameters. We have noted that this scheme gives the perfect agreement with experimental values of lattice constant a , cohesive energy E_c and Bulk modulus B in their solid state. However for the purpose of liquid state calculations, we reparameterized the embedding energy function $F(\rho)$ and pair interaction function $\phi(r)$ following the Rose's EOS that is determined in the next section. In order to obtain effective pair interactions from the EAM, we assume that the third and higher derivatives of the embedding function F are ignored. Thus the atoms interact with the effective pairwise interaction $\phi_{\text{eff}}(r)$ given by

$$\phi_{\text{eff}}(r) = \phi(r) - 2F'(\rho)f(r) \quad (11)$$

where $F'(\rho)$ denotes the first derivative of embedding function.

2.2 Liquid state theory

With the effective pair potential known, integral equations are able to provide us the liquid structure for metals. In our structural calculations, one of the integral equation theory which has shown to be very reliable theory of liquids is VMHNC has been carried out [8-10]. The starting point of most of the integral equation theories of liquids is the Ornstein-Zernike (OZ) equation, which for a homogenous, an isotropic system can be written as

$$h(r) = c(r) + \rho \int d\vec{r}' h(|\vec{r} - \vec{r}'|) c(\vec{r}') \quad (12)$$

which defines the direct correlation function $c(r)$, in terms of the total correlation function, $h(r)=g(r)-1$ where $g(r)$ is the pair distribution function and ρ is the number density. This equation is supplemented by the exact closure relation involving the pair potential $\phi(r)$,

$$g(r) = \exp[h(r) - c(r) - \beta\phi(r) - B(r)] \quad (13)$$

where $\beta = (k_B T)^{-1}$, and $B(r)$ is the bridge function. In this work $B(r)$ is approximated by the use of the analytic solution of the Percus-Yevick (PY) equation for hard sphere (HS), namely $B(r) = B_{PY}(r, \eta)$ [10]. The packing fraction $\eta = \eta(\beta, \rho)$ is variationally determined by minimising the VMHNC configurational free energy at a temperature T , as

$$\frac{\partial f^{VMHNC}(\beta, \rho, \eta)}{\partial \eta} = 0 \quad (14)$$

The value of $\eta = \eta(\beta, \rho)$ thus obtained is used to solve the OZ equation to calculate $g(r)$, the structure factor $S(q)$. The Helmholtz free energy of a system can be written as

$$F_H = F^{ideal} + E(n) + k_B T f^{VMHNC} \quad (15)$$

where F^{ideal} is the ideal gas contribution. $E(n)$ is the structure independent part of the total energy in Eq. (1).

3. Results and discussion

Firstly, we have presented effective interatomic pair potentials based on the Mishin's EAM potential functions for liquids Cu, Ag, Au and Ni. The input parameters, such as the ionic number densities and thermodynamic states for liquids Cu, Ag, Au and Ni are taken from Waseda [16] and given in Table 1. We have determined the parameters of the EAM potential functions by combining the equation for the cohesive energy (Eq. 9), the equation of the equilibrium condition (Eq. 10) and the two equations for the cut-off procedure (Eqs. 5 and 6), and the equation for minimising the configurational free energy (Eq. 14). We must say that we have not fitted the Helmholtz free energy. Following others [5, 6], the set of parameters have been chosen to give the best possible values for the Helmholtz free energy. These results also obtain a good fit to the structure factor. The optimized potential parameters are presented in Table 2. The remaining parameters are the same as in Ref. [1].

Table 1. Input data used in our calculations.

Metal	T(K)	n(atoms/Å ³)	a(Å)	E _c ^{solid} (eV)	E _c ^{liquid} (eV)	B ^{solid} (eV/Å ³)
Cu	1423	0.0755	3.61	3.54	3.110	0.89
Au	1423	0.0526	4.08	3.93	3.484	0.99
Ag	1273	0.0518	4.09	2.85	2.440	0.69
Ni	1773	0.0792	3.52	4.45	3.846	1.22

Fig. 1 shows our potential functions. In Fig. 1a the calculated pair interaction function for Cu in the liquid state is compared with those obtained by Mishin [1]. The computed embedding energy for liquids Cu, Ag, Au and Ni are shown in Fig. 1b. We have also plotted in Fig. 1b, for comparison, the embedding energy derived from the solid state calculations. It is clear in Fig. 1a that the pair potential function in the liquid state becomes softer and the width increases, the position of the principal minimum is displaced to larger values of r . It appears that despite of the different parameterization and fitting schemes, both pair interaction functions look similar except in the short r -range because of the value of r_c in their liquid state calculations are larger than solids. We note that the choice of cut-off procedure affects the behaviour of these functions, particularly nearest neighbour distance.

Table 2. The EAM potential parameters.

Metal	E ₁ (eV)	α ₁ (Å ⁻¹)	r ₀ ⁽¹⁾ (Å)	h(Å)	A	δ(Å)	F ⁽⁰⁾ (eV)	F ⁽²⁾ (eV)
Ni	1.89960×10 ²	2.95699	0.83015	0.10037	3.52	0.86225×10 ⁻²	-2.33335	1.73345
Cu	1.91758×10 ²	2.96758	0.83010	0.10037	3.61	0.86225×10 ⁻²	-2.18235	1.25535
Au	1.94825×10 ²	2.99120	0.82615	0.10037	4.08	0.39225×10 ⁻²	-3.72666	1.15953
Ag	1.93760×10 ²	2.98470	0.82315	0.10037	4.09	0.39225×10 ⁻²	-3.09915	1.14953

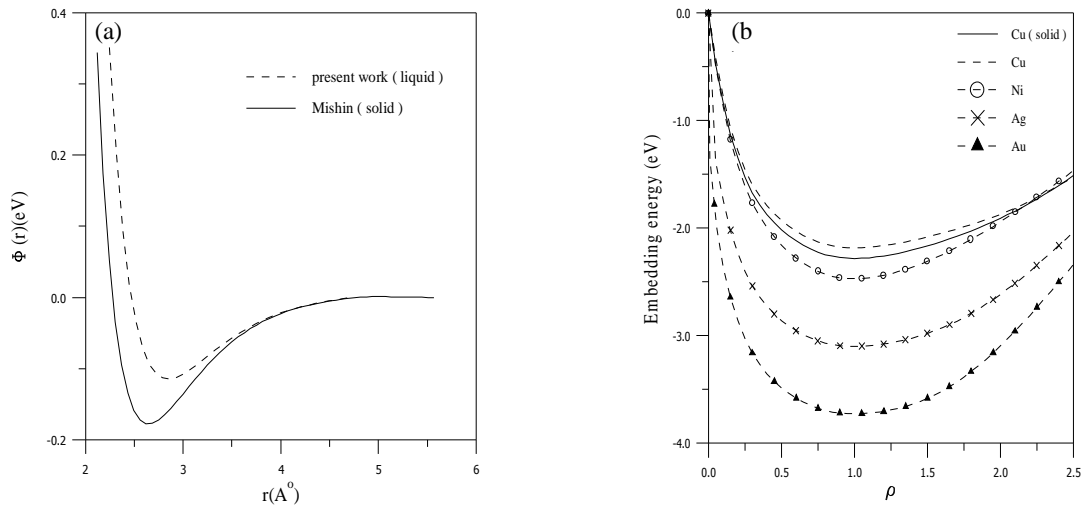


Fig. 1. (a) Pair interaction function for Cu (b) Embedding energy function for liquids Ni, Cu, Ag, and Au.

It can be seen in Fig. 1b that the variations of the embedding energy function found within the group of liquid noble metals follow rather well trends with the periodic table. The increasing atomic volume, going down the column, the obtained embedding energy becomes wider and the position of its minimum towards values which are larger than the atomic radius. The calculated interatomic EAM effective pair potentials for liquids Ni, Cu, Ag, and Au are illustrated in Fig. 2.

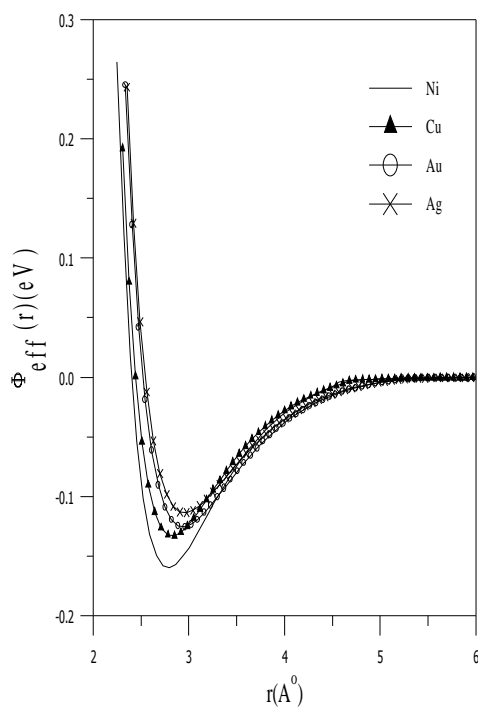


Fig. 2. EAM effective pair potentials.

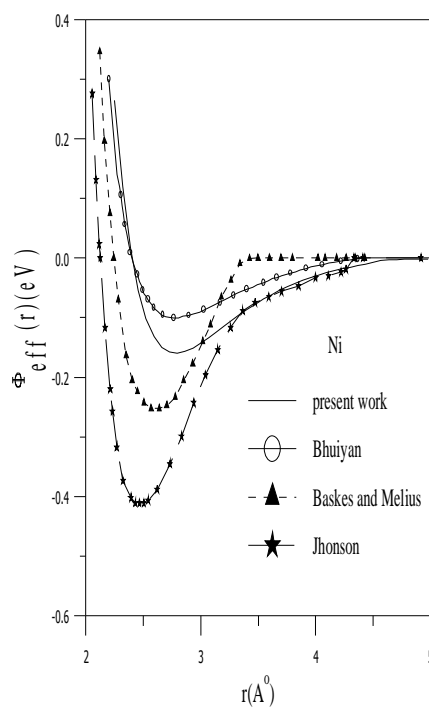


Fig. 3. Comparison of the EAM effective pair potentials for Ni.

It is observed in Fig. 2 that the Mishin's EAM method gives the correct trends as far as the position of the potential is concerned. As we go down column of the Periodic Table, the calculated potential becomes softer and the width increases and the position of the principal minimum towards to larger r values. Fig. 3 shows the computed EAM effective pair potential for liquid Ni in comparing with those obtained by others using different EAM model potentials [1, 5, 17,18]. We have included in Fig. 3 that the effective interatomic pair potential obtained from a new EAM parameterization for liquid transitions metals adopted by Bhuiyan et al. [5]. The EAM derived effective pair potentials of Johnson [17], Baskes and Melius [18] in the solid state are also shown in Fig. 3. It appears that the presented EAM potential functions give rise a deep potential well than Bhuiyan's. It shows more long range character than others.

These effective pair potentials are used as input data in our structural calculations. We have solved the O-Z equation (12) with closure relation (13) using Zerah's algorithm [19]. In Fig. 4 we have presented the calculated static structure factors and pair distribution functions using the VMHNC liquid state theory with the Mishin's EAM effective pair potentials, along with the experimental data of Waseda [16].

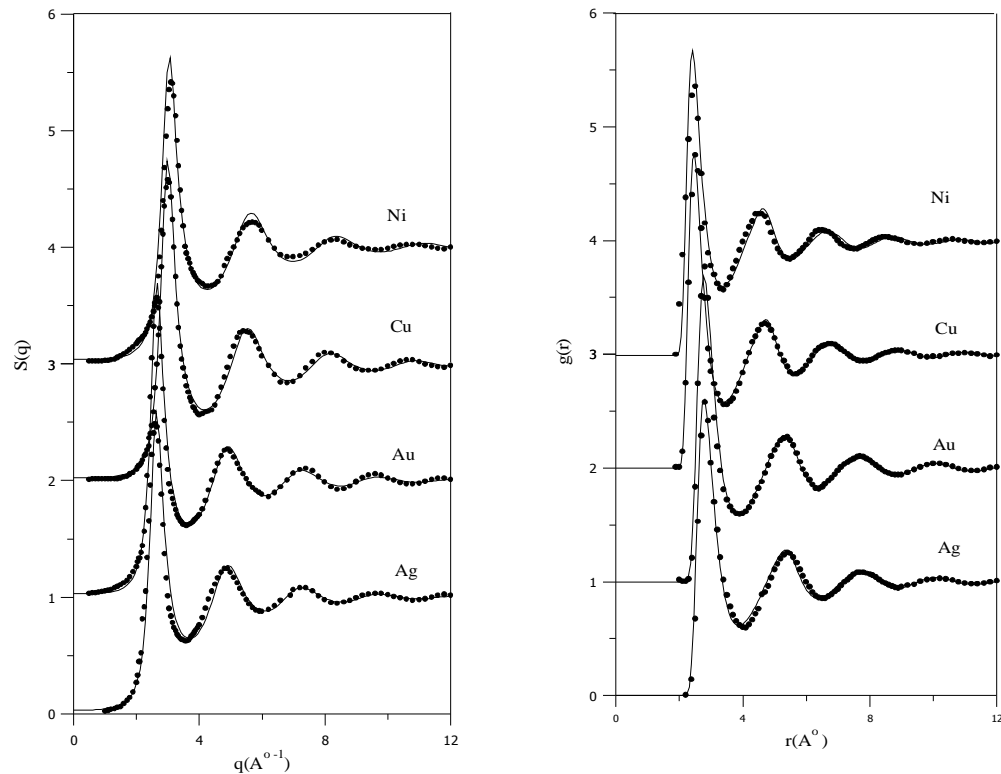


Fig. 4. (a) Static structure factors (b) pair distribution functions for the liquid fcc transition metals near melting. Solid lines show the present results and full circles denote the experimental data from Waseda [16].

In general, we find there is overall good qualitative agreement between calculated and experimental results. However, more details must be given. The calculated $S(q)$ for Ag exhibits a small shift towards the larger q values. The calculations for Cu and Ni tend to overestimate the height of the principal peak of $S(q)$. This difference may be because of the VMHNC theory used in this work or the EAM potential to combined effects of both. However, we believe that this discrepancy is related with the EAM derived effective pair potential. Because the asymptotic behaviour of the potential is reflected in small q behaviour of the liquid structure. As it is well known, the height and position of the principal peak shows a delicate balance between the repulsive and attractive contributions to the effective pair potential. As we indicated above, the calculated EAM pair potential for Ni shows a longer range character than for others.

4. Conclusions

The presented Mishin's embedded – atom method provides a realistic description of the pair interactions in liquid fcc transition metals. These calculations were performed for functions that not only fit to solid data but also liquid state properties. Since $F(\rho)$ and $\phi(r)$ in the liquid state samples are different from those of the solid, we have improved the functional forms of the potentials to obtain a good description of the liquid and still describe the solid accurately. We note that our effective pair potentials show long-range character different from other EAM derived effective potentials for liquids. The structural calculations were carried out using Mishin's-EAM derived effective pair potentials with the VMHNC theory of liquids. Comparison between the results of the VMHNC theory and experimental data show that the Mishin's EAM formalism is capable of providing a good

description of the liquid state. Our results suggest that the effective pair potential based on Mishin's EAM model is a very good approximation for the study of liquid state properties. The thermodynamic properties of liquid transition metals can be computed with these potentials using the VMHNC liquid state theory. The present model is also easy to be generalized to the alloy case. This work will be continued on these lines and will be presented in the near future.

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