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# Molecular dynamics simulation of thermophysical properties of undercooled liquid cobalt

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## Abstract

Molecular dynamics simulations with two different embedded-atom-method (EAM) potentials are applied to calculate the density, specific heat and self-diffusion coefficient of liquid cobalt at temperatures above and below the melting temperature. Simulation shows that Pasianot's EAM model of cobalt constructed on the basis of a hcp structure is more successful than Stoop's EAM model in the framework of a fcc structure in predicting the thermophysical properties of liquid cobalt. Simulations with Pasianot's EAM model indicate that the density fits into  $\rho = 7.49 - 9.17 \times 10^{-4}(T - T_m)$  g cm<sup>-3</sup>, and the self-diffusion coefficient is given by  $D = 1.291 \times 10^{-7} \exp(-48795.71/RT)$  m<sup>2</sup> s<sup>-1</sup>. Dissimilar to the linear dependence of the density and the Arrhenius dependence of the self-diffusion coefficient on temperature, the specific heat shows almost a constant value of  $38.595 \pm 0.084$  J mol<sup>-1</sup> K<sup>-1</sup> within the temperature range of simulation. The simulated properties of liquid cobalt are compared with experimental data available. Comparisons show reasonable agreements between the simulated results from Pasianot's EAM model and experimental data.

## 1. Introduction

Undercooled liquid has aroused great research interest in recent years [1] for two reasons. First, undercooled liquid is not in thermal equilibrium and has not been well known up to now. Second, the rapid solidification of undercooled liquid is an efficient way to produce novel structures such as metallic glass and a new metastable phase, which is normally excluded by a phase diagram. The thermophysical properties of undercooled liquid, such as density, specific heat and self-diffusion coefficient, are of fundamental importance in understanding

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and defining the thermodynamic state of the system [2]. These three parameters can also give some information on the local structure of undercooled liquid [3], and thus can be used to predict the glass transition trend of the liquid [4]. Moreover, to quantitatively predict the processes of crystal nucleation and crystal growth during rapid solidification, one needs the detailed knowledge of these three parameters in an undercooled regime [5, 6]. However, for materials with high melting point and high reactivity, the metastable state of an undercooled liquid is hard to access and keep for a long duration. As a result, there is little experimental data available on these three parameters in an undercooled regime. Accurate knowledge of the thermophysical properties requires not only the further development of experimental techniques, such as the containerless processing technique in combination with the non-contact diagnostic method [2, 6], but also the development of reliable predictive methods.

The molecular dynamics simulation (MDS) with a potential model from the embedded-atom-method (EAM) has been proved to be a powerful approach to the simulation of liquid metals, which was developed two decades ago, and has been successfully applied to simulate the structure, surface and phase transformation of solid or liquid metals [7, 8]. It has also been applied to predict thermophysical properties of liquid metals in some extreme cases [9, 10].

Similar to nickel and iron, cobalt is a ferromagnetic transition metal with wide applications in the aerospace industry. Nevertheless, compared with nickel and iron, cobalt is less well understood. There is a lack of experimental data of specific heat, density and diffusion coefficient of liquid cobalt, especially in the undercooled regime. The purpose of the present work is to carry out simulations on these three parameters, especially in the undercooled regime. The experimental data available are used for comparisons.

## 2. Embedded-atom method

The embedded-atom method (EAM) is a semi-empirical technique for computing the energy of an arbitrary arrangement of atoms. According to the EAM potential model originally developed by Daw and Baskes [11, 12] on the basis of the density function theory and the concept of a quasi-atom [13] or effective-medium approach [14], the energy of an atomic system can be written as

$$E_{\text{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i \neq j} \phi_{i,j}(r_{i,j}) \quad (1)$$

$$\rho_i = \sum_{i \neq j} f_j(r_{i,j}) \quad (2)$$

where  $F_i$  is the energy of embedding atom  $i$  in an electron density  $\rho_i$ ,  $\phi_{i,j}$  a repulsive two-body potential between atoms  $i$  and  $j$ , and  $f_j(r_{i,j})$  the contribution of atom  $j$  to the electron density at atom  $i$  at a distance  $r_{i,j}$  from atom  $j$ .

Two different EAM potentials have been developed in the literature for cobalt. One was constructed by Stoop [15] on the basis of Johnson's EAM model of a face-centred-cubic (fcc) structure [16], and the other was developed by Pasianot *et al* [17] according to cobalt of hexagonal close-packed (hcp) structure. Following Stoop,  $F(\rho)$ ,  $\phi(r)$  and  $f(r)$  are expressed as:

$$f(r) = f_e \left( \frac{r_e}{r} \right)^\beta \quad (3)$$

$$\phi(r) = 2\gamma E_c \left[ \frac{1}{\gamma S_\gamma} \left( \frac{r_e}{r} \right)^\gamma - \frac{1}{\beta S_\beta} \left( \frac{r_e}{r} \right)^\beta \right] \quad (4)$$

$$F(\rho) = -E_c \left\{ 1 + \alpha \left[ \left( \frac{\rho_e}{\rho} \right)^{1/\beta} - 1 \right] \right\} \exp \left[ -\alpha \left( \frac{\rho_e}{\rho} \right)^{1/\beta} - 1 \right] - E_c \left[ \left( \frac{\rho}{\rho_e} \right)^{\gamma/\beta} - \frac{\gamma}{\beta} \frac{\rho}{\rho_e} \right] \quad (5)$$

with

$$S_\beta = \sum_{i=1}^n N_i (r_i/r_e)^{-\beta} \quad (6)$$

$$S_\gamma = \sum_{i=1}^n N_i (r_i/r_e)^{-\gamma} \quad (7)$$

where  $f_e$  is the scaling factor,  $E_c$  the cohesive energy,  $r_e$  the nearest neighbour distance,  $\rho_e$  the equilibrium electron density, and  $r_i$ ,  $N_i$  the radius and the number of atoms in the  $i$ th neighbour shell.

According to Pasianot's EAM model,  $f(r)$  is represented by a Thomas–Fermi screening function

$$f(r) = \exp(-\beta r/a_0)/(r/a_0). \quad (8)$$

The pair interaction is given as a seven-piece cubic polynomial:

$$\phi(r) = \sum_{k=1}^7 A_k (R_k - r)^3 H(R_k - r) \quad (9)$$

where  $H(x)$  is the Heaviside function: if  $x \leq 0$ ,  $H(x) = 0$ ; otherwise,  $H(x) = 1$ .

The embedding function  $F(\rho)$  is numerically fitted to the universal form of cohesive energy of Rose [18]:

$$E(\tilde{a}) = -E_c(1 + \tilde{a}) \exp(-\tilde{a}) \quad (10)$$

with

$$\tilde{a} = 3[\Omega \langle B \rangle / E_c]^{1/2} (a/a_0 - 1) \quad (11)$$

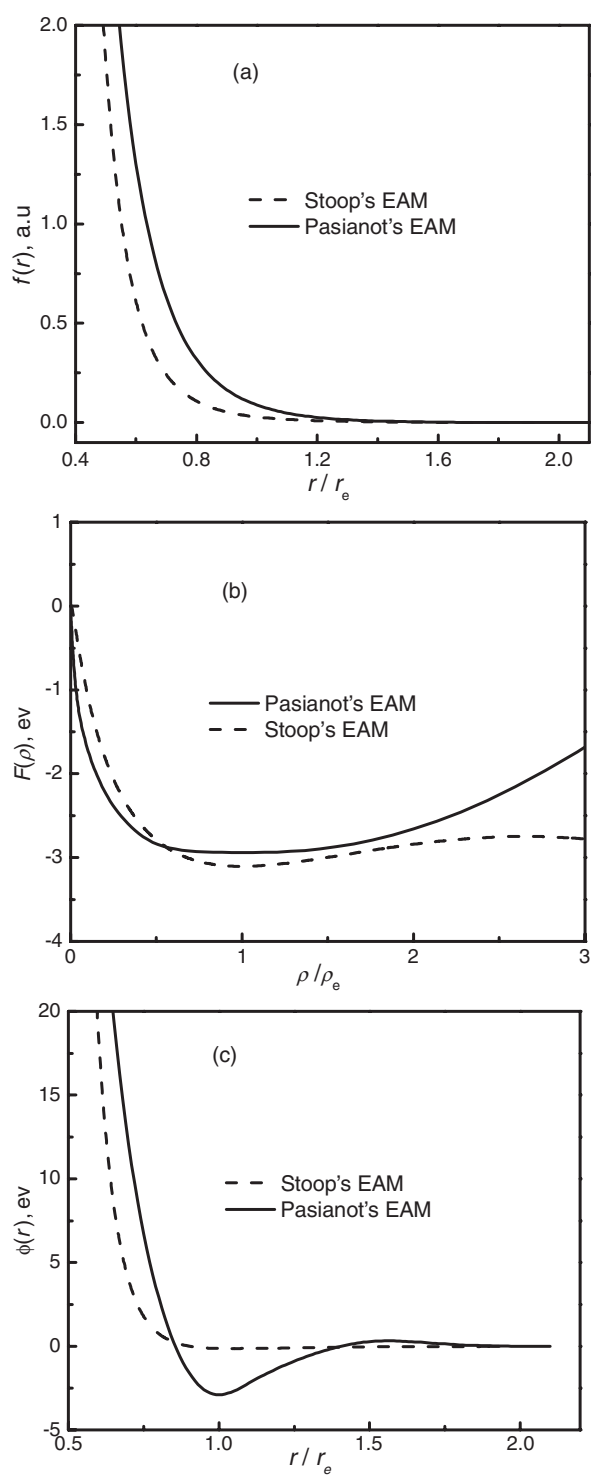
where  $a_0$  is the equilibrium lattice constant,  $a$  is the value of  $a_0$  when the crystal is compressed or expanded,  $a/a_0$  describes the deviation of a crystal from the equilibrium state,  $\langle B \rangle$  is the average (Voigt) bulk modulus, and  $\Omega$  is the equilibrium atomic volume. So that  $F(\rho)$  is properly defined,  $E(\tilde{a})$  is modified after the middle of the sixth and seventh nearest neighbour distance to go smoothly to zero when the expanded crystal has a nearest neighbour distance equal to a cut-off distance,  $r_{\text{cut}} = 2.1a_0$ .

The model parameters used during simulations for Stoop's EAM model and Pasianot's EAM model are listed in tables 1 and 2, respectively. The embedding function, the pair potential and the electron density of these two EAM potentials are illustrated in figure 1.

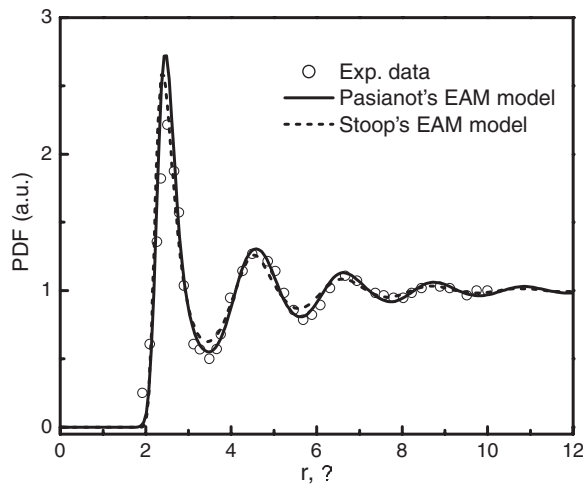
The validity of these two EAM potentials in describing the atomic interactions of liquid cobalt can be illustrated from the good agreement between the simulated pair distribution functions (PDF) at a temperature of 1670 K and the experimental data [19], as presented in figure 2. The PDF is determined from:

$$g(r) = \frac{V \langle n_i(r, r + \Delta r) \rangle}{4\pi r^2 \Delta r N}. \quad (12)$$

Here  $\langle n_i(r, r + \Delta r) \rangle$  is the average number of atoms surrounding the  $i$ th atom in a spherical shell between  $r$  and  $r + \Delta r$ .  $N$  is the total number of atoms involved in the system under consideration and  $V$  is the volume of system.



**Figure 1.** Illustration of Pasianot's EAM and Stoop's EAM potentials: (a) electron density,  $f(r)$ ; (b) embedding function,  $F(\rho)$ ; (c) pair potential,  $\phi(r)$ .



**Figure 2.** Simulated and experimental PDF of liquid cobalt at a temperature of 1670 K.

**Table 1.** The model parameters for Stoop's EAM.

Model parameter								
$b$ (Å)	$\Omega$ (Å <sup>3</sup> )	$\rho_e$	$f_e$	$S_\gamma$	$S_\beta$	$\gamma$	$\beta$	$\alpha$
2.503	11.09	0.3956	0.02849	12.806	13.886	7.745	5.933	5.004

**Table 2.** The model parameters for Pasianot's EAM model ( $R_i$  in units of  $a_0$ ,  $a_0$  in Å,  $E_c$  and  $A_i$  in eV).

Model parameter			
$R_1$	2.1	$A_1$	0.263 789 17
$R_2$	1.8	$A_2$	-0.707 060 79
$R_3$	1.7	$A_3$	-1.801 508 45
$R_4$	1.5	$A_4$	2.698 423 62
$R_5$	1.3	$A_5$	-0.350 486 95
$R_6$	1.1	$A_6$	32.524 020 0
$R_7$	1.0	$A_7$	-4.109 211 22
$a_0$	2.507	$E_c$	4.39

### 3. Simulation details

The density, specific heat and self-diffusion coefficient are simulated applying the MD simulation method under constant pressure and constant temperature ( $NPT$  ensemble). Andersen's  $NPT$  algorithm is used during simulations. During simulation, the pressure is set to zero. At the beginning of the simulation, 4000 atoms were arranged in a face-centred-cubic box subject to periodic boundary conditions in three directions. The time step was  $5.0 \times 10^{-15}$  s. In order to get the equilibrium liquid state in the simulation, the system started at 2000 K, which is well above the melting point. This temperature was kept constant for 50 000 steps. Then the quenching process with a cooling rate of  $4 \times 10^{11}$  K s<sup>-1</sup> was carried out to calculate the enthalpy  $H$  and density  $\rho$  at 100 K intervals of temperature. At each temperature, 30 000 steps were carried out for equilibrium. Then 20 000 additional steps were

taken to calculate the enthalpy and density. The simulation was stopped at 1200 K, which is 566 K lower than the melting point. Since the quenching process is very fast, the metal stays in an undercooled liquid state.

According to Andersen's *NPT* algorithm, the box length can be obtained from the feedback of pressure to zero. Thus, the density can be derived from its definition.

Specific heat can be determined from the differential of the enthalpy:

$$C_p = \frac{dH(T)}{dT} = \frac{d(E + PV)}{dT} \quad (13)$$

where  $E$  is the internal energy, which is the sum of the kinetic energy and the potential energy,  $P$  the pressure, and  $V$  the volume of the system.

As to the self-diffusion coefficient  $D$ , there are two calculation methods [20]. One method is to calculate from the generalized-Einstein (GE) equation

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_{j=1}^N [r_j(t) - r_j(0)]^2 \right\rangle \quad (14)$$

where  $r_j(0)$  is the initial position of the  $j$ th particle and  $r_j(t)$  the position of  $j$ th particle at some later time  $t$ .

The other method is to calculate the self-diffusion coefficient from the Green-Kubo (GK) equation:

$$D = \frac{1}{3N} \int_0^\infty \left\langle \sum_{j=1}^N \vec{v}_j(0) \cdot \vec{v}_j(\tau) \right\rangle d\tau \quad (15)$$

where  $\vec{v}_j(0)$  is the initial velocity vector for the  $j$ th particle and  $\vec{v}_j(\tau)$  the velocity vector at some later time  $\tau$ .

Due to the uncertainty introduced by the integral of infinite time in the Green-Kubo equation, we employ the GE equation to calculate the self-diffusion coefficient. In order to obtain reliable average values for equation (13), we utilized the algorithm of overlapping-time-interval correlation averages proposed by Rapaport [20]. The results for the self-diffusion coefficient were calculated using an average of 20 individual correlation functions, each lasting 25 ps.

#### 4. Simulation results

Figure 3 presents the density data obtained from simulations with different EAM potentials for pure liquid cobalt. The simulation is limited within a temperature range of 1200–2000 K, which corresponds to a undercooling of 566 K ( $0.32T_m$ ) and a superheating of 234 K ( $0.13T_m$ ). In this temperature range, the system is kept as liquid. When the temperature is less than 1200 K, from Pasianot's EAM model, the system will crystallize. Stoop's EAM model predicts that:

$$\rho = 7.47 - 7.7 \times 10^{-4}(T - 1766) \text{ g cm}^{-3}. \quad (16)$$

The density predicted from Pasianot's EAM model is represented by:

$$\rho = 7.49 - 9.17 \times 10^{-4}(T - 1766) \text{ g cm}^{-3}. \quad (17)$$

Obviously, the difference of the simulated densities between the two EAM potentials in the stable liquid above the melting point is very small. However, Pasianot's EAM model predicts a larger value than Stoop's EAM model in the undercooled regime. Moreover, the deeper the undercooling, the larger the difference.

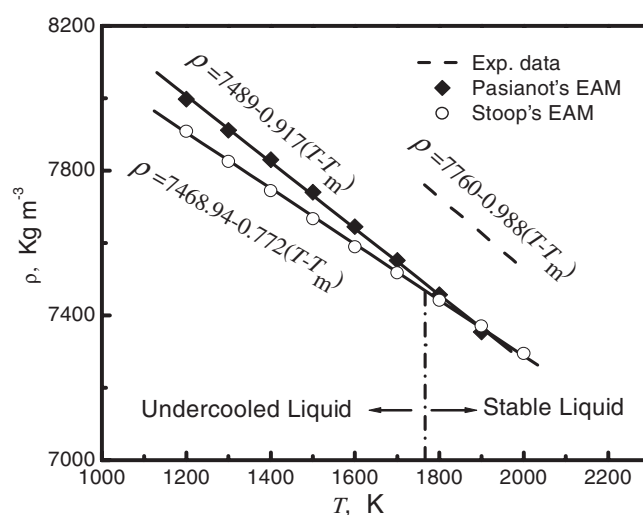


Figure 3. Density of liquid cobalt versus temperature.

The experimental data from *Smithells Metals Reference Book* [21] were also added to figure 3, which are given by:

$$\rho = 7.76 - 9.88 \times 10^{-4}(T - 1766) \text{ g cm}^{-3}. \quad (18)$$

Comparison indicates that both EAM potentials underestimate the density of stable liquid cobalt by about 3–4%. For the density temperature dependence,  $d\rho/dT$ , Pasianot's EAM model predicts a more reasonable value than Stoop's EAM model. The difference between the simulated  $d\rho/dT$  from Pasianot's EAM model and experimental value is about 7%, whereas for Stoop's EAM model the difference is over 22%. Owing to the lack of density data in the undercooled regime, the deviation between the simulated and measured density below the melting point cannot be evaluated.

The simulation results for the enthalpy  $H$  are shown in figure 4. Apparently, the enthalpy has a linear dependence on temperature. Data analysis shows that from Stoop's EAM model

$$H = -6.94 \times 10^6 + (550.7 \pm 3.29)T \text{ J kg}^{-1}, \quad (19)$$

and from Pasianot's EAM model

$$H = -7.15 \times 10^6 + (654.9 \pm 1.42)T \text{ J kg}^{-1}. \quad (20)$$

This means that the heat capacity changes very little in the whole simulated temperature range. Stoop's and Pasianot's EAM potentials produce heat capacities of  $32.509 \pm 0.194$  and  $38.595 \pm 0.084 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. According to *The Physical Properties of Liquid Metals* edited by Iida [22], the specific heat of stable liquid cobalt above the melting point is  $40.38 \text{ J mol}^{-1} \text{ K}^{-1}$ . Wang *et al* [5] measured the specific heat of undercooled liquid cobalt in the undercooling range of 0–227 K using an electromagnetic levitation method, and the experimental value is  $40.6 \text{ J mol}^{-1} \text{ K}^{-1}$ . Apparently, the predicted result of Pasianot's EAM model is quite close to the experimental value with a difference less than 5%. Stoop's EAM model underestimates the specific heat of liquid cobalt too much, the difference being 20%.

Figure 5 illustrates the dependence of mean square displacement (MSD) on the time of liquid cobalt at different temperatures. Noticeably, MSD is a linear function of time. Thus the self-diffusion coefficient can be calculated conveniently from the first derivative of MSD.



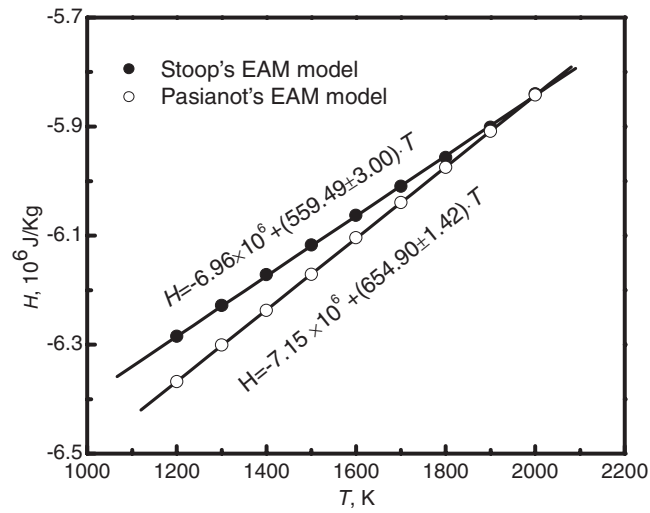


Figure 4. Calculated enthalpy of liquid cobalt versus temperature.

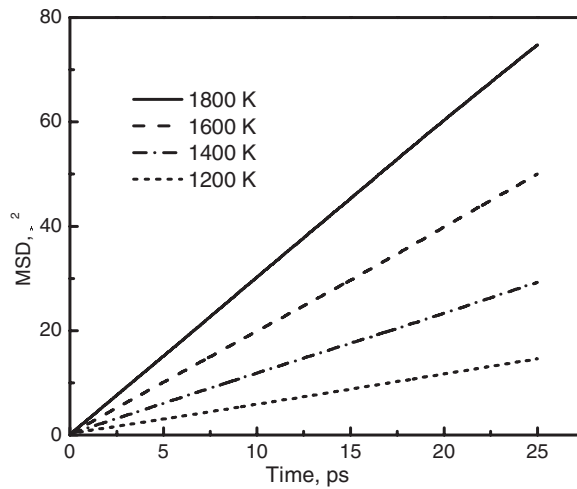


Figure 5. Mean squared displacement of liquid cobalt at different temperatures.

Shown in figure 6 are the results of the self-diffusion coefficient of liquid cobalt as a function of temperature. The open circles are the data calculated in the current simulation from Pasianot's EAM model, which are expressed as:

$$D = 1.291 \times 10^{-7} \exp\left(-\frac{48795.71}{RT}\right) \text{ m}^2 \text{ s}^{-1}. \quad (21)$$

The open squares represent the self-diffusion coefficients calculated from Stoop's EAM model, which are expressed as:

$$D = 6.315 \times 10^{-8} \exp\left(-\frac{31715.12}{RT}\right) \text{ m}^2 \text{ s}^{-1} \quad (22)$$

where  $R$  is the gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

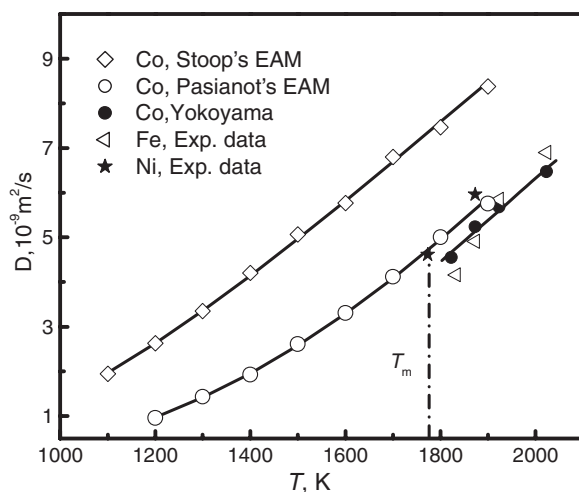


Figure 6. Dependence of self-diffusion coefficient of liquid cobalt on temperature.

Due to the lack of experimental data on stable and undercooled liquid cobalt, we can only compare the simulated results with those predicted from theoretical models or the experimentally measured data of the neighbouring elements of cobalt in the Elemental Periodical Table, such as iron and nickel. In figure 6, the solid circles are the self-diffusion coefficients of stable liquid cobalt predicted by Yokoyama [23] based on a hard-sphere description, and the open triangles and solid stars are the experimental self-diffusion coefficients of iron and nickel [23], respectively. It can be seen that the self-diffusion coefficient of Pasianot's EAM model is close to Yokoyama's work above the melting point. Moreover, the results of Pasianot's EAM model do not deviate greatly from the experimental values of liquid iron and nickel. Therefore, the simulated result from Pasianot's EAM model is reasonable. Stoop's EAM model seems to overestimate the self-diffusion coefficient of liquid cobalt too much.

From the investigations on the density, specific heat and self-diffusion coefficient, it can be concluded that Pasianot's EAM model is more successful than Stoop's EAM model in describing the atomic interactions in liquid cobalt. This is understandable, since Stoop constructed the EAM of cobalt in the framework of the fcc structure with the data at low temperature. However, the fcc phase is a high-temperature phase and it will transform into the hcp phase through a martensitic phase transformation at a temperature around 693 K. Although hcp and fcc structures have the same number density and similar stacking behaviour, they have different neighbour distance and atoms in a given neighbour shell. Consequently, the atomic interaction of cobalt cannot be described by Stoop's EAM model in the framework of the fcc structure as well as Pasianot's EAM model in the framework of the hcp structure.

In order to analyse the influence of the computational domain on the results, runs with 500, 1372 and 2048 atoms are carried out. It was found that among different systems the difference of density is less than 0.09%, and the difference of the enthalpy is less than 0.05%. Therefore, the size effect is not noticeable, and a system of 4000 atoms is enough to obtain reasonable results.

## 5. Conclusions

The density, specific heat and self-diffusion coefficient of liquid cobalt in a wide temperature range, especially in the undercooled regime, have been predicted by molecular dynamics

simulations with two different EAM potentials. The results indicate that although both EAM potentials describe the PDF sufficiently well, only Pasianot's EAM potential is capable of delivering reasonable thermophysical data. This means that Pasianot's EAM model in the framework of the hcp structure is more successful than Stoop's EAM model in the framework of the fcc structure in modelling the atomistic interactions in stable and undercooled liquid cobalt. At temperatures of 1200–2000 K, Pasianot's EAM model predicts a density of  $\rho = 7.49\text{--}9.17 \times 10^{-4}(T - T_m) \text{ g cm}^{-3}$ . The absolute value and temperature dependence of the density are in good agreement with experimental results above the melting point, within a deviation of less than 4% and 7%, respectively. The simulated self-diffusion coefficient based on Pasianot's EAM model shows an Arrhenius temperature dependence represented by  $D = 1.291 \times 10^{-7} \exp(-48\,795.71/RT) \text{ m}^2 \text{ s}^{-1}$ , which agrees well with the approximated values from empirical expressions. Compared with the density and self-diffusion coefficient, specific heat shows no obvious temperature dependence in the temperature range of 1200–2000 K. The predicted specific heat of  $38.595 \pm 0.084 \text{ J mol}^{-1} \text{ K}^{-1}$  from Pasianot's EAM model agrees well with the experimental results, with a deviation of less than 5%. Simulations show that the molecular dynamics simulation method with an appropriate EAM inter-atomic potential model can predict the thermophysical properties of undercooled liquid metals quantitatively.

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